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Experimental Investigation of Imbibition in Oil-Wet Carbonates Under Low IFT Conditions

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Experimental Investigation of Imbibition in Oil-Wet Carbonates Under Low IFT Conditions

by

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Thesis

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Dedication

To my Mother and Father.

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Abstract

Experimental Investigation of Imbibition in Oil-Wet Carbonates Under Low IFT Conditions

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The University of Texas at Austin, 2016

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Natural reservoir drives and waterflooding in naturally fractured carbonate reservoirs with an oil-wet matrix generate very low oil production. Surfactants enhance oil recovery in these reservoirs by altering wettability and reducing interfacial tension (IFT). The main purpose of this research was to determine how to scale up low IFT surfactant imbibition from the lab to fractured, oil-wet carbonate reservoirs.

A series of imbibition experiments were conducted using cores with different horizontal (i.e. diameter) and vertical (i.e. height) dimensions. Their fractional oil recoveries (% OOIP) were systematically measured to better understand how to scale up the surfactant imbibition process. There was a particular need to perform experiments using cores with larger horizontal dimensions since almost all previous experiments in the literature used cores with a small diameter, typically 3.8 cm. The core diameters in this study varied from 3.8 to 20 cm. The traditional static imbibition experimental method was adapted and modified by periodically flushing out fluids surrounding the cores inside the cells to better estimate the oil recovery, including the significant amount of oil

produced as an emulsion. The high performance surfactant formulations for the oils used on in this study were developed using microemulsion phase behavior tests. These surfactants gave ultra-low IFT (on the order of 0.001 dynes/cm) at optimal salinity and good aqueous stability. Although most of the experiments used ultra-low IFT formulations, experiments using higher IFT (on the order of 0.1 dynes/cm) formulations were also performed for comparison. Even for the higher IFT experiments, the capillary pressure is very small compared to gravity and viscous pressure gradients. In addition, experiments were done to understand the role of other variables on oil recovery, such as matrix permeability, surfactant and co-solvent concentrations, microemulsion viscosity, and oil viscosity.

A simple analytical model was developed to predict the oil recovery as a function of vertical and horizontal fracture spacing, rock and fluid properties, and time. The model and experimental data are in good agreement considering the many simplifications made to derive the model. Both experimental data and the model showed that the oil recovery was lower for cores with larger horizontal and vertical dimensions. However, the decrease was not proportional to an increase in these dimensions. The scaling implied by the model is significantly different than the traditional scaling groups in the literature.

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Chapter 1: Introduction

Naturally fractured carbonate reservoirs contain a significant fraction of the world's oil reserves. The carbonate rocks that make up these reservoirs typically were formed from biological activities and water evaporations. They consist of predominantly calcite ($CaCO_3$) and dolomite ($CaMg(CO_3)_2$) minerals. Due to the complex reservoir heterogeneity and large variations in petrophysical properties (e.g. porosity and permeability) between the matrix and fractures, recovering oil from a carbonate reservoir is very challenging.

Water preferentially displaces oil present in the fractures of a fractured reservoir with relatively little oil displaced from the matrix by viscous forces depending on the permeability ratio of the fracture and matrix, fracture spacing, how well the fractures are connected, and other factors. Water is imbibed into the matrix by capillary forces when the matrix is not oil-wet. However, around 80% of the fractured reservoirs are oil-wet to mixed-wet carbonates (Goudarzi et al. 2012), so little if any water is imbibed into the matrix and hence little if any oil is produced from the matrix. Therefore, there is a great need for enhanced oil recovery methods for oil-wet fractured carbonate reservoirs. The current EOR methods include the injection of carbon dioxide, air, nitrogen, steam, polymer, and surfactant.

Anionic surfactants that generate low to ultra-low IFT were used in this research. Correctly scaling up these lab results to the field requires the understanding of the physics of the surfactant imbibition process. Static imbibition cells have been traditionally used to assess the effectiveness of surfactant formulations in recovering oil by measuring the oil recovery as a function of time. In this research, the imbibition cells were modified to allow the fluids surrounding the cores to be periodically flushed out to better estimate the

oil recovery, including the significant amount of oil produced as emulsion. The oil recovery data were then compared to examine the effect of changing rock and fluid properties such as core dimensions to understand the underlying physics.

Despite many studies reported in the literature, insufficient data are available to answer the important question about the scale-up of the surfactant imbibition process. No systematic studies of surfactant imbibition using cores with a diameter greater than 3.8 cm had been reported when this study commenced. The experiments done as part of this research were designed specifically to address the scaling question. Cores of five different sizes were used in the experiments, covering an aspect ratio (i.e. height/diameter) range of 0.9 to 8. The rate of imbibition was expected to be slower for cores with a larger diameter, and that was confirmed by the new experiments. Experiments were also done to understand the role of other variables such as rock permeability, IFT, surfactant and co-solvent concentrations, and microemulsion viscosity. A total of 29 imbibition experiments are reported in this thesis.

Li et al. (2016) recently developed a simplified analytical imbibition model to predict the oil recovery as a function of time for low IFT surfactant imbibition. They compared the model predictions with the oil recovery data measured as part of this research with the emphasis on testing the model for cores of different sizes to understand how the process scales up.

At low IFT, capillary pressure is negligible. Imbibition is driven by the difference in the gravity head between the surfactant solution outside the core and the oil inside the core, which induces a small horizontal pressure gradient. A microemulsion forms when the surfactant mixes with oil and water inside the core. The microemulsion phase has very different properties than the oil and water phases. For example, the microemulsion viscosity is typically higher than that of oil and water. The larger viscosity increases the

horizontal pressure gradient relative to the vertical pressure gradient in the oil phase. An attempt was made to model both the gravity and pressure gradients in the core with a simple model. The detailed assumptions and derivation of this model are given in Appendix A. Comparisons with the new experimental data for cores of different sizes are shown in the results and discussion section.

Chapter 2: Background and Literature Review

This chapter provides the background information and literature review on surfactant imbibition research. First, the basic concepts of the surfactants used in EOR and their properties are presented. Then, the surfactant imbibition experiments and scaling laws in the literature are discussed.

2.1 Surfactants in EOR and Their Properties

A surfactant molecule is a surface-active agent that lowers the surface energy barrier between two immiscible phases. A surfactant molecule is also known as an amphiphile because it consists of a polar hydrophilic (water-liking) head and a non-polar hydrophobic (oil-liking) tail. The hydrophilic/lipophilic balance (HLB), an empirical number, indicates the relative tendency of a surfactant to dissolve in oil or water, with low HLB numbers assigned to surfactants that are more soluble in oil.

Several important surfactant characteristics make a good surfactant candidate for EOR processes. First, the surfactant needs to generate low to ultra-low IFT between oil and water by having a strong molecular interaction with them. The surfactant's strong interaction with oil and water relative to mineral surfaces reduces surfactant adsorption. Lastly, molecular branching of the surfactant's hydrophobic tail prevents the formation of viscous structures or rigid interfaces such as gels and liquid crystals, inhibiting the surfactant from smoothly flowing through pore throats.

The four main types of surfactants are anionic, cationic, nonionic, and amphoteric (also called zwitterionic). As these names suggest, the classification is based on the polar-group identity of the surfactant head. Since the imbibition experiments conducted in this research only used anionic surfactants, this section mostly reviews and discusses this group of surfactants. Due to their low costs and comparatively low adsorption on

sandstones, anionic surfactants are the most common type of surfactant used for EOR. When dissolved in an aqueous solution (brine), the anionic surfactant separates into a metal cation, typically sodium, and a monomer. If the surfactant concentration is increased, some of the monomers form colloidal aggregates, known as micelles, by directing their hydrophobic tails inward and hydrophilic heads outward. The total surfactant concentration eventually reaches a point called the critical micelle concentration (CMC), beyond which any additional increase in the total surfactant concentration causes an increase only in the micelle concentration but not the monomer concentration. When the aqueous solution containing surfactant(s) contacts an oleic phase, a fraction of the surfactant molecules begins to saturate the interface between the two phases (hydrophobic tails in the oleic phase and hydrophilic heads in the aqueous phase).

2.1.1 Microemulsion Phase Behavior

Under certain conditions, a thermodynamically stable fluid called a microemulsion forms when brine, oil, and surfactant(s) are mixed. Its structure does not change with time nor does it depend on how it is prepared once equilibrated. The microemulsion phase behavior is sensitive to the brine salinity when anionic surfactants are used. At low brine salinity, the mixture of brine, oil, and surfactant(s) at equilibrium separates into an excess oil phase on top and an oil-in-water microemulsion phase on bottom. As the salinity of the brine increases, the microemulsion phase transitions from a Type I (described in the previous sentence) to Type III and lastly to Type II microemulsion. This phase transition was first reported by Winsor in 1954. In the Type III microemulsion, the middle microemulsion phase is bicontinuous. The Type II

microemulsion is exactly opposite that of the Type I, with a water-in-oil microemulsion phase on top and an excess brine phase on bottom.

2.1.2 IFT and Phase Behavior

Healy and Reed (1974) showed that IFT strongly correlates with oil and water solubilization ratios. The water solubilization ratio σ_{13} is the ratio of the volume of water solubilized to the volume of surfactant in the microemulsion phase. Similarly, the oil solubilization ratio σ_{23} is the ratio of the volume of oil solubilized to the volume of surfactant in the microemulsion phase. The microemulsion phase is assumed to contain all of the surfactant(s). Huh (1979) derived a theoretical equation calculating the IFT using solubilization ratios,

$$\gamma_{i3} = \frac{0.3}{\sigma_{i3}^2}$$

Where γ_{i3} is the IFT (dynes/cm or mN/m) between phase i and the microemulsion phase 3 and σ_{i3} is the solubilization ratio (dimensionless) of phase i in the microemulsion phase 3. The subscript numbering system for the phases is such that 1 is water (brine), 2 is oil, and 3 is microemulsion. The IFT can be accurately estimated from equilibrium phase behavior data without the need for difficult IFT measurements that are subject to large errors, especially when dark crude oils are used or the temperature and pressure are high, among other complications. In addition, qualitative indications of viscosity and other useful observations can be made at the same time as the phase behavior observations are made on the same samples. For these reasons, it has become less common to measure IFT.

In Type I microemulsion, the IFT value γ_{23} is defined but not the value γ_{13} because the excess water phase does not exist. All of the water is solubilized in the lower microemulsion phase. As salinity increases and Type I transitions into Type III

microemulsion, more oil is solubilized in the microemulsion phase. The oil solubilization ratio σ_{23} increases (Figure 2.1), and thus the IFT γ_{23} decreases (Figure 2.2). Both IFT values γ_{23} and γ_{13} are defined in Type III microemulsion, for both the excess oil and water phases exist. At a particular salinity in the Type III region, equal and large amounts of oil and water are solubilized. The IFT values γ_{23} and γ_{13} are equal and the lowest at this optimal salinity. As salinity increases further and Type III transitions into Type II microemulsion, less water is solubilized in the microemulsion phase. The water solubilization ratio σ_{13} decreases (Figure 2.1), and thus the IFT γ_{13} increases (Figure 2.2). In Type II microemulsion, the IFT value γ_{13} is defined but not the value γ_{23} because the excess oil phase does not exist. All of the oil is solubilized in the upper microemulsion phase.

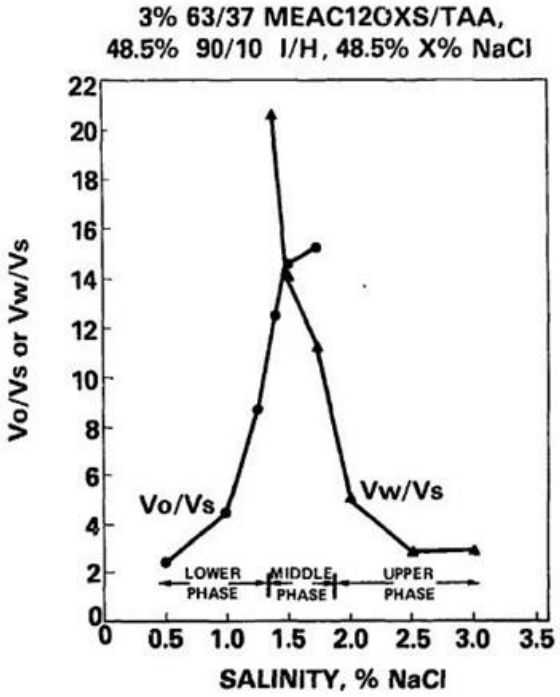


Figure 2.1: Solubilization ratio (Vo/Vs is σ_{23} and Vw/Vs is σ_{13}) versus salinity (Healy and Reed 1976).

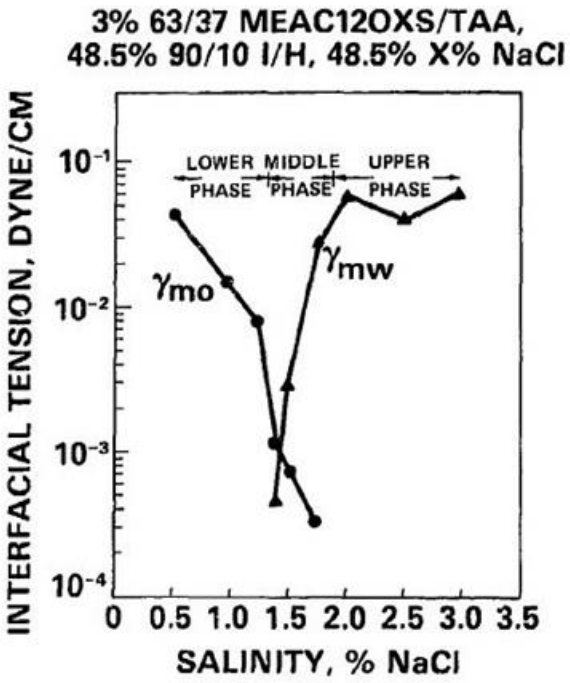


Figure 2.2: IFT (γ_{mo} is γ_{23} and γ_{mw} is γ_{13}) versus salinity (Healy and Reed 1976).

Solubilization ratios of 10 or greater generate ultra-low IFTs in the range of 0.003 dynes/cm or less, which are four or more orders of magnitude less than the typical IFT of 30 dynes/cm between oil and water. Microemulsions at optimal salinity are believed to be near the tricritical point where the three phases become chemically indistinguishable and thus exhibit ultra-low IFTs between all phases (Green and Willhite 1998).

2.1.3 Wettability Alteration

When an aqueous solution containing surfactant penetrates and flows into the pore spaces of a rock matrix, some of the surfactant molecules adsorb onto the solid surfaces of the grain minerals, thus changing the wettability of the rock. All types of surfactants (i.e. anionic, cationic, nonionic, and amphoteric) alter the wettability of the grain minerals to some degree. However, their wettability-alteration mechanisms are

different. The wettability-alteration mechanisms of anionic and cationic surfactants will be reviewed.

One measure of wettability is capillary pressure. Oil pressure in the pores of a rock is higher than the water pressure (positive capillary pressure) when the rock is water wet and lower than the water pressure (negative capillary pressure) when the rock is oil wet. Water imbibes into the rock only over the range of saturations corresponding to a positive capillary pressure. If the rock is oil wet at all saturations, then no water imbibes. Thus it is often desirable to change the wettability of the rock from oil-wet to water-wet, where the positive capillary forces favor the spontaneous imbibition of water.

The conventional view of wettability assumes that for an oil-wet rock, the solid surfaces are at least partially coated with negatively charged organic materials from the crude oil (mostly carboxylic groups). Electrostatic repulsion may prevent the desorption of these adsorbed organic materials by means of anionic surfactants. Instead, the hydrophobic tails of the anionic surfactants adsorb onto the hydrophobic surface of the rock (already adsorbed with a layer of organic materials from the crude oil) to form a surfactant double layer as shown in Figure 2.3 (Standnes and Austad 2000b). However, the surfactant double layer does not permanently alter the wettability of the rock. The change in wettability is fully reversible due to the weak hydrophobic interactions (bonds) between the anionic surfactant tails and the organic materials. If the core is then immersed in oil, the previously imbibed surfactant solution may be displaced by the oil (Chen et al. 2000). However, in some cases it has been observed that a highly optimized anionic surfactant formulation completely solubilizes the oil on the surface rendering it water wet.

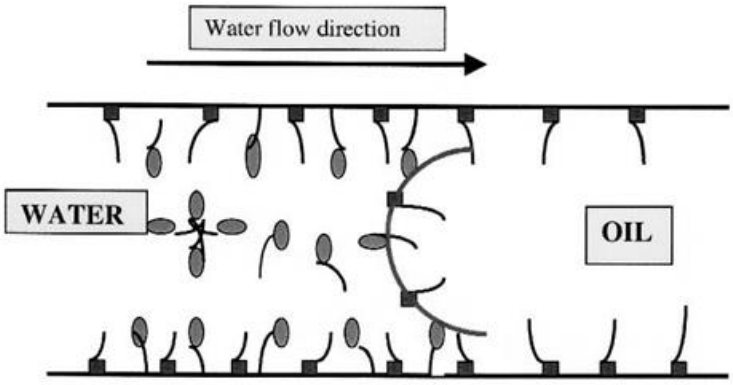


Figure 2.3: Wettability alteration of anionic surfactants by the formation of a surfactant double layer in a pore. Ellipses represent anionic surfactants, and squares represent adsorbed organic materials from crude oil (Standnes and Austad 2000b).

Due to electrostatic forces of attraction, cationic surfactants interact with the adsorbed negatively charged organic materials from the crude oil. At the interface between oil, water, and rock inside a pore (Figure 2.4), the adsorbed organic material gets desorbed from the rock surface by forming an ion-pair with the cationic surfactant monomer (Standnes and Austad 2000b). Stabilized by hydrophobic interactions, the ion-pairs are either dissolved in the oil phase as a ratio of 1:1 complexes or in the micelles of the water phase (Standnes and Austad 2000b). The rock permanently becomes more water-wet once the adsorbed negatively charged organic materials are released from the rock surfaces (Standnes and Austad 2000b).

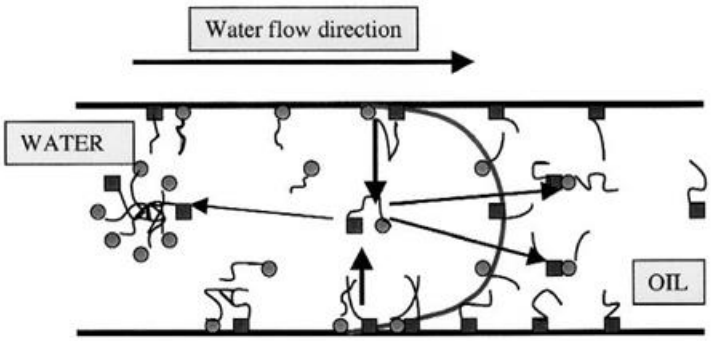


Figure 2.4: Wettability alteration of cationic surfactants by the desorption of organic materials (represented by squares) and their formation of ion-pairs with cationic surfactants (represented by circles) in a pore (Standnes and Austad 2000b).

2.2 STATIC SURFACTANT IMBIBITION EXPERIMENTS

A wide range of surfactants have been evaluated over the past 30 years for EOR by performing experiments using static imbibition cells. These studies have included tests with cationic surfactants, nonionic surfactants, and anionic surfactants.

Austad et al. (1998) used the cationic surfactant Dodecyl Trimethyl Ammonium Bromide (DTAB) and chalk cores with a diameter of 3.7 cm. About 65% of the oil was recovered after 90 days of surfactant imbibition. Standnes and Austad (2000) used tetra alkyl ammonium surfactant to change the wettability of chalk. About 70% of the oil was recovered after 30 days of spontaneous imbibition. Standnes et al. (2002) conducted imbibition experiments using cores with a diameter of 3.8 cm. They tested an ethoxylated alcohol and a cationic surfactant (C12TAB). The C12TAB gave about 40-45% oil recovery compared to only 10% for the ethoxylated alcohol. Xie et al. (2005) tested both a cationic surfactant and a nonionic surfactant in dolomite cores with diameters of 2.54 cm and 3.8 cm.

Seethepalli et al. (2004) identified several anionic surfactants that change the wettability of carbonate surfaces from oil wet to intermediate- or water-wet as well as or

better than the cationic surfactant DTAB. Their spontaneous imbibition tests were performed using oil-wet carbonate cores with a diameter of 3.8 cm. About 50% of the oil was recovered using 0.05 wt% anionic surfactant solutions. Various dilute anionic surfactant solutions (<0.1 wt%) have been shown to recover 40-70% of the oil from oil-wet limestone cores with a diameter of 3.8 cm (Adibhatla and Mohanty 2008; Gupta et al. 2008; Gupta and Mohanty 2010).

Sagi et al. (2013) used 0.5% tridecyl-propoxy-sulfate and dolomite cores with a diameter of 2.54 and 3.8 cm diameter. Kathel and Mohanty (2013) show that the use of dilute (0.1 wt %) anionic surfactant solution with a large number of ethoxy groups can recover up to 68% of the oil from tight (~10 μD) oil-wet/mixed-wet sandstone reservoir cores with a diameter of 2.54 cm diameter.

While the above experiments were all conducted using static imbibition cells, some recent work to evaluate surfactants for fractured reservoirs was done using dynamic corefloods (Parra 2016). Parra (2016) hypothesized that a viscous microemulsion can increase the oil recovery from naturally fractured reservoirs by inducing pressure gradients transverse to the fractures. To test the hypothesis, two ultra-low IFT surfactant floods were first performed using fractured Silurian dolomite cores with a permeability contrast between the fracture and matrix of 2,500 and 5,000 (Parra 2016). Hydrolyzed polyacrylamide polymer was then added to the injected surfactant solution to test the effect of viscous forces on the oil recovery from the fractured cores (Parra 2016). The oil cut increased from about 1 to 7%, and the pressure drop increased from about 0.5 to 1.0 psi/ft (Parra 2016). The injection of viscous surfactant-polymer solution demonstrated the importance of viscous forces in fractured carbonate cores. Next, four low to ultra-low surfactant floods were performed using fractured Texas cream limestone cores (Parra 2016). Viscous microemulsions were used as mobility control agents instead of polymer,

and the viscosity of microemulsion was varied by changing the salinity of the surfactant solution. Increasing the microemulsion viscosity from 0.5 to 75 cp increased the oil recovery from fractured oil-wet limestone cores by 40% OOIP (Parra 2016). Therefore, Parra (2016) concluded that viscous microemulsions have the potential to greatly increase the oil recovery from fractured, oil-wet carbonate reservoirs.

2.3 Scaling Laws of Spontaneous Imbibition

The challenge remains regarding how to scale up these results to the field. Many scaling groups have been proposed for gravity-dominated imbibition (Du Prey, 1978; Hagoort, 1980; Li and Horne, 2006; Chen, 2014; Hui et al., 2014). None of these scaling groups have been adequately validated. In fact, experimental data for cores with larger diameters were not even available for such validation. Some experimental data for cores with different heights were available, but it was not clear the proposed scaling groups accurately correlate all of the experimental results.

Chapter 3: Methodology

3.1 General Materials

3.1.1 Cores

Texas cream limestone and Silurian dolomite cores were used in this study. From visual observation, the Texas cream limestone cores appeared to be more homogeneous than the Silurian dolomite cores. Small vugs could sometimes be found on the surface of the Silurian dolomite cores. A rock mineralogy analysis was done on a sample of the Texas cream limestone using X-ray diffraction. The XRD results are shown in Table 3.1. The mineralogy analysis was not done on the Silurian dolomite. The brine permeability of the Texas cream limestone cores ranged from 5 to 54 md with an average of 18 md, and the porosity ranged from 0.23 to 0.34 with an average of 0.27. The brine permeability of the Silurian dolomite cores ranged from 30 to 63 md with an average of 50 md, and the porosity ranged from 0.12 to 0.17 with an average of 0.15.

Table 3.1: Texas cream limestone mineralogy analysis done by K-T GeoServices using X-ray diffraction.

Whole Rock Mineralogy (Weight Percent)	
Quartz	0.4
K-Feldspar	0
Plagioclase	0
Calcite	99
Dolomite	0
Fe-Dolomite	0
Siderite	0
Pyrite	0
Hematite	0
Total Phyllosilicates	0.6
Total	100

Cores of five different sizes were used in the imbibition experiments as shown in Figure 3.1. The aspect ratio (i.e. height/diameter) of the cores ranged from 0.9 to 8. All of the cores were cylindrical in shape except for one rectangular core. The rectangular core had a square base of 20.2 cm side and a height of 9.5 cm. The core dimensions and properties are shown in Table 4.1.

Figure 3.1: Cores of different horizontal and vertical dimensions. Foot-long ruler for scale.

3.1.2 Oils

McElroy and RBD dead oils and Oregon Basin and SAMA surrogate oils were used in this study. The Oregon Basin dead oil was diluted with 20 wt% decalin to make the surrogate oil. The SAMA dead oil was diluted with 10 wt% toluene to make the surrogate oil. Only the Oregon Basin oil was slightly reactive with alkali to form soap. The oil densities and viscosities are shown in Table 4.1.

3.1.3 Anionic Surfactants and Co-Solvents

The anionic surfactants used in this study were obtained from Shell Chemical Company and Stepan Chemical Company. Some anionic surfactants were synthesized in

our laboratory from chemicals obtained from Harcros Chemicals. The co-solvents used in this study were obtained from Harcros Chemicals. The surfactants and co-solvents are listed in Table 4.2.

3.2 MODIFIED IMBIBITION CELL

Imbibition experiments have traditionally been done using imbibition cells (Ghedan 1989; Sharma and Mohanty 2013). The classic imbibition cell, from bottom to top, consists of a large glass cylinder with its top end gradually tapered and connected to a long, narrow glass tube as shown in Figure 3.2. The core sits inside and at the bottom of the glass cylinder surrounded by a stationary fluid filled to a certain height. Over time, the cumulative oil expelled from the core is collected at the top in the long, narrow glass tube. The oil recovery is measured by observing an interface between the expelled oil and the imbibing fluid. The classic imbibition cell is closed both at the top and bottom ends, and the imbibing fluid is flowed into the cell only at the beginning of the experiment. No displacement of the fluids out of the cell occurs, making the imbibition experiment a completely static test.

Figure 3.2: The classic imbibition cell is closed both at the top and bottom ends. The fluids inside the cell could not be flushed out regularly for analysis.

In this study, surfactant formulations with a high solubilization ratio at the optimal salinity were tested. Almost all of the produced oil was solubilized by the surfactant solution surrounding the core, forming an emulsion inside the imbibition cell. Therefore, the oil recovery could not be measured by observing the interface between the oil and water. Figure 3.3 shows photographs of the emulsion inside the cell at different times of the surfactant imbibition. The classic imbibition cell with closed end-pieces did not allow the emulsion to be extracted regularly to measure its oil content. A 1/8 inch diameter hole with 1/16 inch Swagelok female NPT connection was drilled in each end-piece. A 1/8 inch Swagelok tube fitting to 1/16 inch male NPT connection was then attached to each piece. Using gravity feed, fresh surfactant solution flowed into the cell

through the bottom end-piece and displaced the emulsion out through the top as shown in Figure 3.4. The modification allowed the oil production to be measured regularly by flushing out the emulsion for analysis. The annular volume between the cell wall and the core was minimized to reduce the volume of surfactant solution needed to flush out the emulsion. Imbibition cells of different sizes were used in this study. The design and construction of the cells were done at the glass shop in the Welch Hall and the machine shop in the Chemical and Petroleum Engineering building at the University of Texas at Austin.

Figure 3.3: Photographs of an imbibition cell at different times during surfactant imbibition. An emulsion was formed inside the cell as the produced oil was solubilized by the surfactant solution. The emulsion became more oil-rich as the time increased.

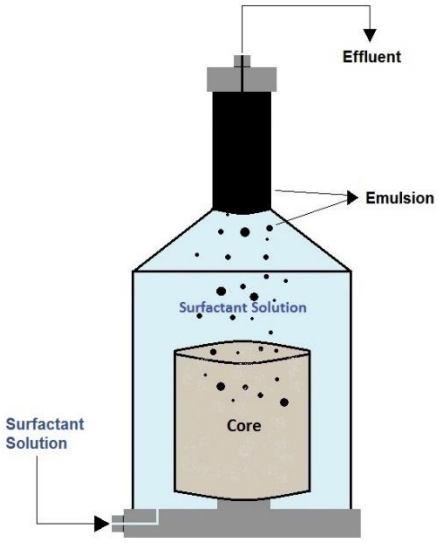


Figure 3.4: Schematic diagram of the modified imbibition cell. Fresh surfactant solution was flowed into the base of the cell using gravity feed to flush out the emulsion through the top of the cell.

Materials Used to Make the End-Pieces of the Imbibition Cell

The material of the end-pieces, the bottom base and the top cap, of the glass imbibition cell was polytetrafluoroethylene (PTFE). The cell was tested at 75°C. Due to the different expansion rates of the glass and PTFE, the base expanded faster than the outer layer of glass screwed onto the base, causing the glass to break at the point where it contacted the PTFE. Consequently, the bottom of the base was made hollow to reduce the volume of expansion.

3.3 Phase Behavior Experiments

Phase behavior experiments were performed to identify good surfactant formulations (shown in Table 4.2) for the oils at experimental temperature. Mixtures of oil, brine, surfactants, and co-solvents were made and sealed in 5 ml glass pipettes for salinity scans. The detailed experimental procedure could be found in Zhao et al. (2008),

Levitt et al. (2009), Flaaten et al. (2009), and Yang et al. (2010). Both emulsion tests and solubilization ratio data versus salinity curves were used to determine the optimal salinity. The surfactant formulations that produced low to ultra-low IFT and reached equilibrium quickly were selected for microemulsion viscosity measurements and imbibition experiments. The aqueous surfactant solution was tested for clarity and stability up to at least the optimal salinity at the experimental temperature. After the fluids had equilibrated, phase volumes were measured and used to determine the oil and water solubilization ratios. The IFT between the oil and microemulsion and the water and microemulsion phases was calculated from the oil and water solubilization ratios using the Huh's equation (Huh 1979).

Large microemulsion samples were made at the desired salinities determined from the salinity scans for each surfactant formulation. After the samples had equilibrated, the microemulsion phase was extracted using a syringe with a long needle to measure the microemulsion viscosity. The viscosity measurements were done using ARES-LS1 and LS-300 rheometers following the procedure in Walker et al. (2012) and Tagavifar et al. (2016).

3.4 Experimental Procedure

The imbibition experiments were conducted using the following procedure.

1. The core was oven dried at about 100 °C for about 12 hours to ensure that there was no liquid in the pores.
2. The mass of the dry core was measured.
3. The core was sealed inside a container and checked for leaks.
4. The core was evacuated using a vacuum pump and checked for leaks.
5. The core was fully saturated with oil at 23 °C for about 12 hours.

6. The core was placed in a sealed container surrounded by oil and aged (for typically 7 to 14 days) at the experimental temperature to render it oil-wet.
7. The mass of the core after aging was measured. The pore volume and porosity of the core were determined from the mass difference of the core before and after oil saturation.
8. The core was immersed in NaCl brine (same salinity as the surfactant solution in step 9) to be tested inside the imbibition cell at the experimental temperature. All sides of the core were open to imbibition. Brine imbibition usually occurred quickly and stopped after about 24 hours. The core was immersed in brine for one day to observe oil recovery.
9. After completion of the brine imbibition process, the core was immersed in surfactant solution to be tested inside the imbibition cell at the experimental temperature. All sides of the core were open to imbibition.
10. Fresh surfactant solution was flowed into the cell using gravity feed to displace the emulsion in the cell at appropriate times (Figure 3.4). The emulsion was flushed out about once per day when the oil production was high. The emulsion was flushed out less frequently when the oil production was low. The emulsion was collected in volumetric flasks (50, 100, or 250 ml).
11. The volume of oil in the emulsion was measured using the method described in section 3.5 Method to Measure Oil Production.
12. The oil recovery was recorded with time.

13. After completion of the surfactant imbibition process, the mass of the core was measured. The final oil recovery was determined from the mass difference of the core before and after surfactant imbibition.
14. The core was cleaned inside a coreholder at 23 °C by injecting several pore volumes of toluene to remove the remaining oil and then several pore volumes of methanol to remove the toluene and adsorbed surfactant.
15. Several pore volumes of 40,000 ppm NaCl brine was injected into the cleaned core to measure its brine permeability at 23 °C.

3.5 Method to Measure Oil Production

Almost all of the oil was expelled from the core as emulsion. The salinity of each effluent sample was first increased by adding NaCl. This was done to increase the accuracy of measurements by increasing the density difference between the oil and brine. Then the effluent sample was placed inside ~60 °C oven for 12 hours. Figure 3.5 shows the effluent sample before and after treatment.

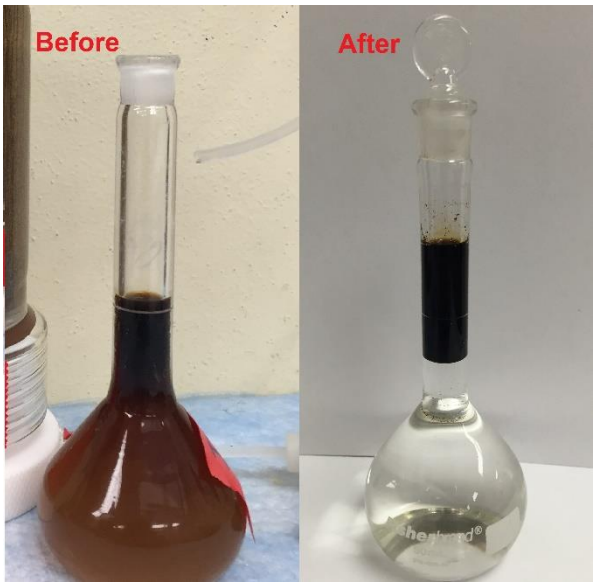


Figure 3.5: Effluent sample in a 50 ml volumetric flask before and after treatment.

To establish the relationship between the volume fraction of oil in the emulsions and the density of the emulsions and to quantify measurement errors, 50 ml emulsion control samples were prepared with different oil volume fractions by mixing known volumes of oil and surfactant solution. The emulsion samples were prepared using surfactant formulations 2 and 7 at the optimal salinity in Table 4.2. The volume fractions of oil represented the values measured in the effluent samples of the imbibition experiments.

The density of the emulsion was assumed to be a linear function of the volume fraction of oil in the emulsion according to the equation $\rho_e = C_o\rho_o + \rho_w(1 - C_o)$, where ρ_o and ρ_w are the densities of oil and brine, respectively, and C_o is the volume fraction of oil in the emulsion. The densities of the emulsion, oil, and brine in each sample were measured and used to calculate the volume fraction of oil in each emulsion. The volume of oil in each emulsion sample is then just the measured volume of the emulsion sample times the volume fraction of oil in the sample. Table 3.2 and Figure 3.6 compare the measured volume of oil in the emulsion control samples with the known volume of oil added to each sample. The difference between the measured and known volumes of oil ranged from -0.18 to 0.11 ml with an average of 0.01 ml. This same method was used to measure the oil volume from all of the imbibition experiments.

Table 3.2: Comparison of measured volume of oil with known volume of oil.

Surfactant Formulation	Control Sample #	Measured Density of Emulsion (g/ml)	Measured Density of Brine (g/ml)	Measured Density of Oil (g/ml)	Measured Volume of Oil (ml)	Known Volume of Oil (ml)	Volume Difference (ml)
Formulation 2	1	1.034	1.059	0.872	0.18	0.10	0.08
	2	1.026	1.059	0.871	0.21	0.20	0.01
	3	1.013	1.062	0.871	0.40	0.40	0.00
	4	0.995	1.057	0.870	0.60	0.60	0.00
	5	0.988	1.062	0.872	0.78	0.80	-0.02
	6	0.991	1.057	0.871	0.82	1.0	-0.18
Formulation 7	7	1.028	1.069	0.865	0.21	0.10	0.11
	8	1.018	1.067	0.868	0.23	0.20	0.03
	9	0.994	1.069	0.872	0.43	0.40	0.03
	10	0.976	1.072	0.872	0.65	0.60	0.05
	11	0.959	1.068	0.873	0.81	0.80	0.01

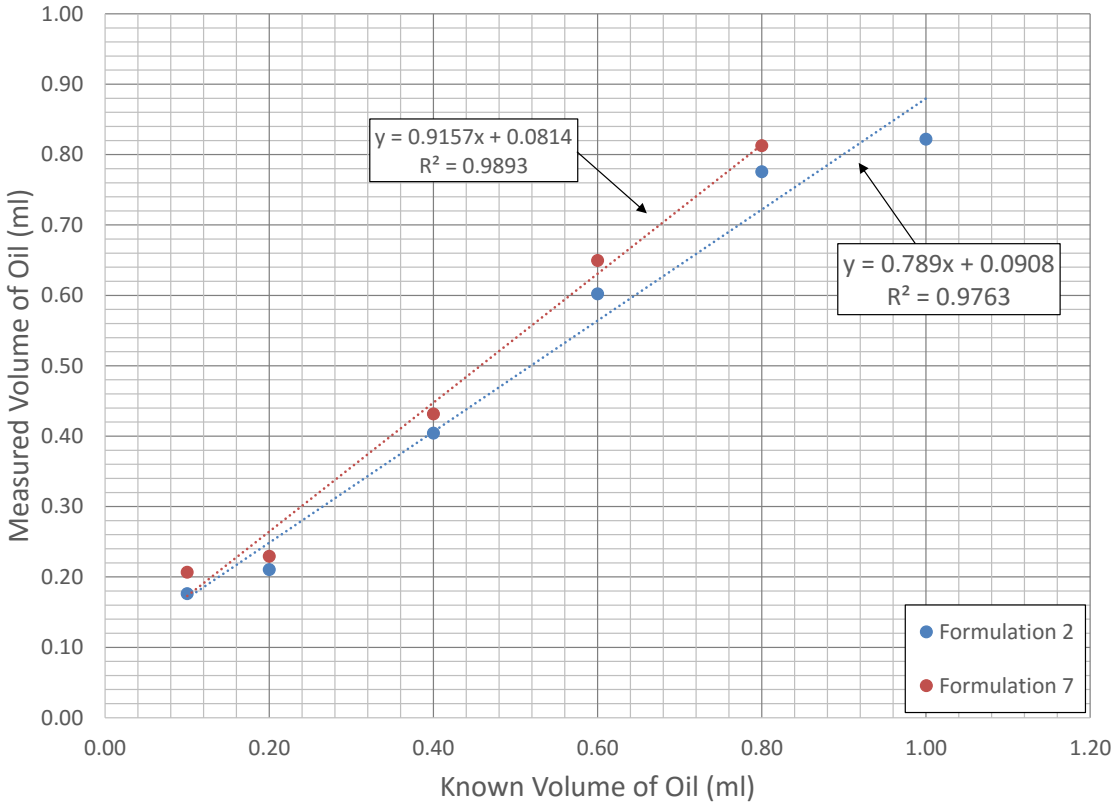


Figure 3.6: Measured volume of oil versus known volume of oil.

Chapter 4: Experimental Results and Discussion

The experimental results are presented and discussed in this chapter. The chapter begins by describing the fluid properties and microemulsion phase behavior of the surfactant formulations used in the imbibition experiments. Table 4.1 shows the experimental parameters such as the core dimensions for all the imbibition experiments (organized by duplicate experiments, core dimensions, and oil). The effect of these parameters on the oil recovery is presented and discussed. Next, the experimental uncertainties are discussed. Lastly, the experimental results are compared with data from the literature.

Table 4.1: Summary of spontaneous imbibition experiments.

Experiment	Rock Type	Diameter	Height	Porosity	Brine Perm	Temp	Oil	Oil Density	Oil Visc.	ME Visc.	Surfactant	Salinity	Phase Type	Surf Sol Density
IE #		cm	cm		md	ºC		g/ml	cp	cp	Formulation #	ppm TDS		g/ml
21	Texas Cream Limestone	3.76	9.55	0.278	7	23	McElroy dead	0.871	12.6	45	2	40000	III	1.027
25	Texas Cream Limestone	3.77	9.78	0.321	47	23	McElroy dead	0.871	12.6	45	2	40000	III	1.027
49	Texas Cream Limestone	3.76	9.83	0.276	8	23	McElroy dead	0.871	12.6	45	2	40000	III	1.027
22	Texas Cream Limestone	10.80	9.43	0.233	7	23	McElroy dead	0.871	12.6	45	2	40000	III	1.027
26	Texas Cream Limestone	10.80	9.35	0.239	7	23	McElroy dead	0.871	12.6	45	2	40000	III	1.027
28	Texas Cream Limestone	20.2*	9.50	0.264	26	23	McElroy dead	0.871	12.6	45	2	40000	III	1.027
29	Texas Cream Limestone	3.77	29.60	0.264	21	23	McElroy dead	0.871	12.6	45	2	40000	III	1.027
45	Texas Cream Limestone	3.76	29.40	0.258	10	23	McElroy dead	0.871	12.6	45	2	40000	III	1.027
47	Texas Cream Limestone	9.80	29.23	0.237	11	23	McElroy dead	0.871	12.6	45	2	40000	III	1.027
31	Texas Cream Limestone	3.77	9.26	0.261	8	23	McElroy dead	0.871	12.6	21	7	50000	III	1.034
34	Texas Cream Limestone	3.79	10.01	0.251	18	23	McElroy dead	0.871	12.6	21	7	50000	III	1.034
23	Texas Cream Limestone	3.78	9.42	0.253	8	23	McElroy dead	0.871	12.6	---	4	45000	III	1.031
24	Texas Cream Limestone	3.77	9.57	0.246	5	23	McElroy dead	0.871	12.6	---	3	30000	III	1.016
33	Texas Cream Limestone	3.78	10.03	0.244	11	23	McElroy dead	0.871	12.6	1	2	27500	I	1.019
46	Texas Cream Limestone	3.75	9.90	0.245	9	23	McElroy dead	0.871	12.6	1	2	10000	I	1.007
35	Texas Cream Limestone	3.77	9.57	0.344	44	23	McElroy dead	0.871	12.6	---	5	33000	III	1.020
48	Texas Cream Limestone	3.76	9.86	0.258	9	23	McElroy dead	0.871	12.6	---	6	37500	III	1.025
17	Silurian Dolomite	3.80	10.06	0.139	---	23	McElroy dead	0.871	12.6	---	1	27500	III	1.014
18	Silurian Dolomite	3.79	9.85	0.121	---	23	McElroy dead	0.871	12.6	---	1	27500	III	1.014
19	Silurian Dolomite	3.80	10.00	0.134	58	23	McElroy dead	0.871	12.6	45	2	27500	III	1.014
30	Silurian Dolomite	3.80	10.25	0.162	63	45	Oregon Basin surrogate	0.904	7	25	8	43000	III	1.040
32	Texas Cream Limestone	3.77	9.43	0.251	---	23	RBD dead	0.863	11	20	9	58500	III	1.058
44	Texas Cream Limestone	3.75	9.83	0.255	---	23	RBD dead	0.863	11	20	9	58500	III	1.058
36	Silurian Dolomite	3.79	9.91	0.167	---	78	SAMA surrogate	0.880	7	20	10	80000	III	1.062
37	Silurian Dolomite	3.78	9.99	0.157	30	78	SAMA surrogate	0.880	7	20	10	80000	III	1.062
40	Texas Cream Limestone	3.76	9.37	0.316	14	78	SAMA surrogate	0.880	7	20	10	80000	III	1.062
41	Texas Cream Limestone	3.76	9.32	0.330	41	78	SAMA surrogate	0.880	7	---	10	20000	I	1.016
42	Texas Cream Limestone	3.76	9.66	0.329	54	78	SAMA surrogate	0.880	7	20	11	75000	III	1.059
43	Texas Cream Limestone	3.76	9.77	0.318	---	78	SAMA surrogate	0.880	7	---	11	20000	I	1.016

*Horizontal length of square base.

4.1 Microemulsion Phase Behavior

Microemulsion phase behavior tests were used to develop the surfactant formulations for the oils used in this study. The surfactant formulations used for each oil are listed in Table 4.2.

Table 4.2: Surfactant formulations.

Formulation #	Surfactant Formulation	Oil	Temperature (°C)
1	0.85 wt% C12-13-13PO-Sulfate 0.15 wt% C15-18 IOS 1.0 wt% IBA	McElroy dead	23
2	0.85 wt% C12-13-13PO-Sulfate 0.15 wt% C15-18 IOS 1.0 wt% Phenol-1PO-2EO	McElroy dead	23
3	0.85 wt% C12-13-13PO-Sulfate 0.15 wt% C15-18 IOS 0 wt% Phenol-1PO-2EO	McElroy dead	23
4	0.85 wt% C12-13-13PO-Sulfate 0.15 wt% C15-18 IOS 2.0 wt% Phenol-1PO-2EO	McElroy dead	23
5	0.2125 wt% C12-13-13PO-Sulfate 0.0375 wt% C15-18 IOS 0.25 wt% Phenol-1PO-2EO	McElroy dead	23
6	0.425 wt% C12-13-13PO-Sulfate 0.075 wt% C15-18 IOS 0.5 wt% Phenol-1PO-2EO	McElroy dead	23
7	0.3 wt% C20-24IOS 0.4 wt% Ole C18-35PO-10EO-sulfate 0.3 wt% 2-Ethylhexanol-7PO-sulfate 1.0 wt% IBA-1PO-2EO	McElroy dead	23
8	0.5 wt% TDA-13PO-Sulfate 0.5 wt% C20-24-IOS 0.5 wt% Phenol-1PO-5EO	Oregon Basin surrogate	45
9	0.1 wt% TDA-13PO-Sulfate 0.2 wt% C20-24-IOS 0.2 wt% TDA-45PO-10EO-Sulfate 0.25 wt% 2-Ethylhexanol-7PO-Sulfate	RBD dead	23
10	0.5 wt% C28-25PO-45EO-COO- 0.2 wt% C15-18-IOS 0.3 wt% C19-28-IOS 1 wt% EDTA	SAMA surrogate	78
11	0.5 wt% C28-25PO-45EO-COO- 0.2 wt% C15-18IOS 0.3 wt% C19-28IOS 0 wt% EDTA	SAMA surrogate	78

Surfactant Formulation 1

The surfactant formulation is 0.85 wt% C12-13-13PO-Sulfate, 0.15 wt% C15-18-IOS, and 1.0 wt% IBA. It formed a stable microemulsion with the McElroy dead oil at 23 ºC, the experimental temperature. A salinity scan was done by adding NaCl to deionized water and using 30% oil volume fraction. Figure 4.1 shows the solubilization ratios of oil and water at different salinities after 85 days of equilibration. The observations of viscous phases in the pipettes and the slow equilibration time due in part at least to the low temperature made the microemulsion phase behavior readings difficult. Based on the emulsion test, the optimal salinity was 27,500 ppm NaCl. The IFT between the microemulsion and excess oil and brine phases was ultra-low at and near the optimal salinity. The aqueous surfactant solution was clear and stable up to 35,000 ppm NaCl for at least 85 days. The microemulsion viscosity was not measured.

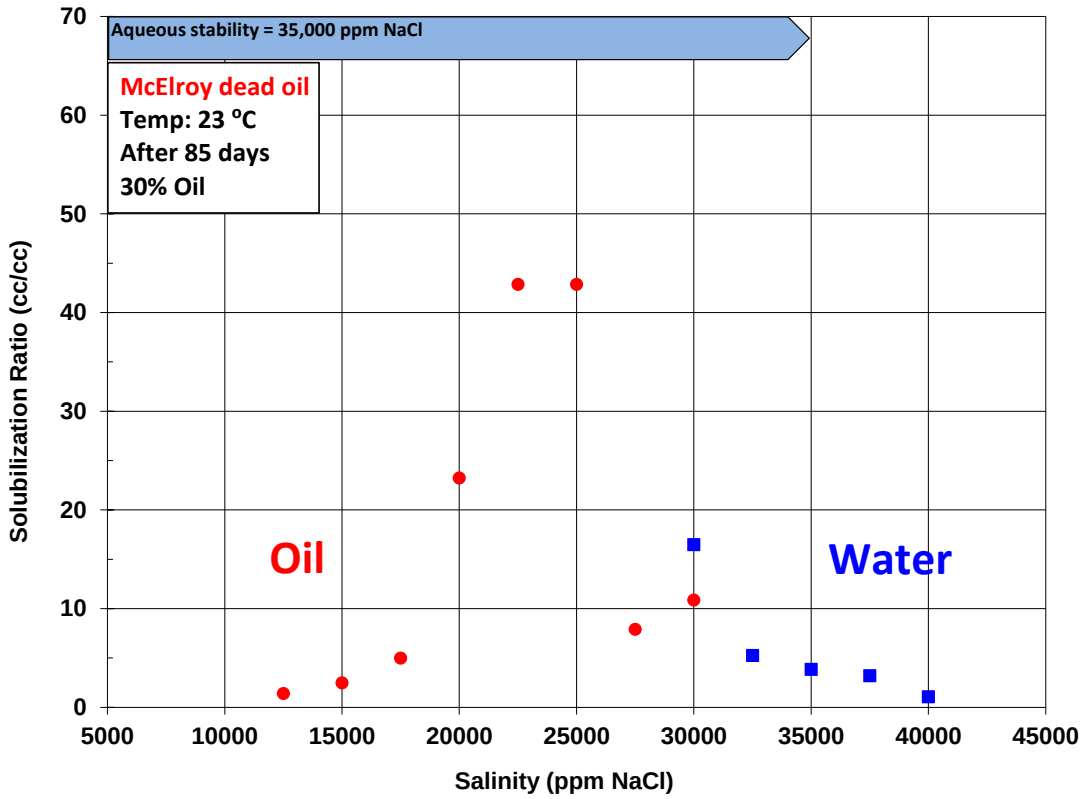


Figure 4.1: Solubilization ratios of oil and water for the 0.85 wt% C12-13-13PO-Sulfate, 0.15 wt% C15-18-IOS, and 1.0 wt% IBA surfactant formulation. Based on the emulsion test, the optimal salinity was about 27,500 ppm NaCl.

Surfactant Formulation 2

The surfactant formulation is 0.85 wt% C12-13-13PO-Sulfate, 0.15 wt% C15-18-IOS, and 1.0 wt% Phenol-1PO-2EO. It formed a stable microemulsion with the McElroy dead oil at 23 ºC, the experimental temperature. A salinity scan was done by adding NaCl to deionized water and using 30% oil volume fraction. Figure 4.2 shows the solubilization ratios of oil and water at different salinities after 354 days of equilibration. The solubilization ratio at the optimal salinity of about 42,000 ppm NaCl was about 13. The IFT at the optimal salinity was estimated to be approximately 1.8×10^{-3} dynes/cm using the solubilization ratio of 13 in the Huh's equation (Huh 1979). The emulsion test

indicated the lowest IFT was at 40,000 ppm NaCl. The aqueous surfactant solution was clear and stable up to 45,000 ppm NaCl for at least 354 days. The microemulsion viscosity at the optimal salinity was 45 cp at 23 ºC, about 3.6 times higher than the oil viscosity.

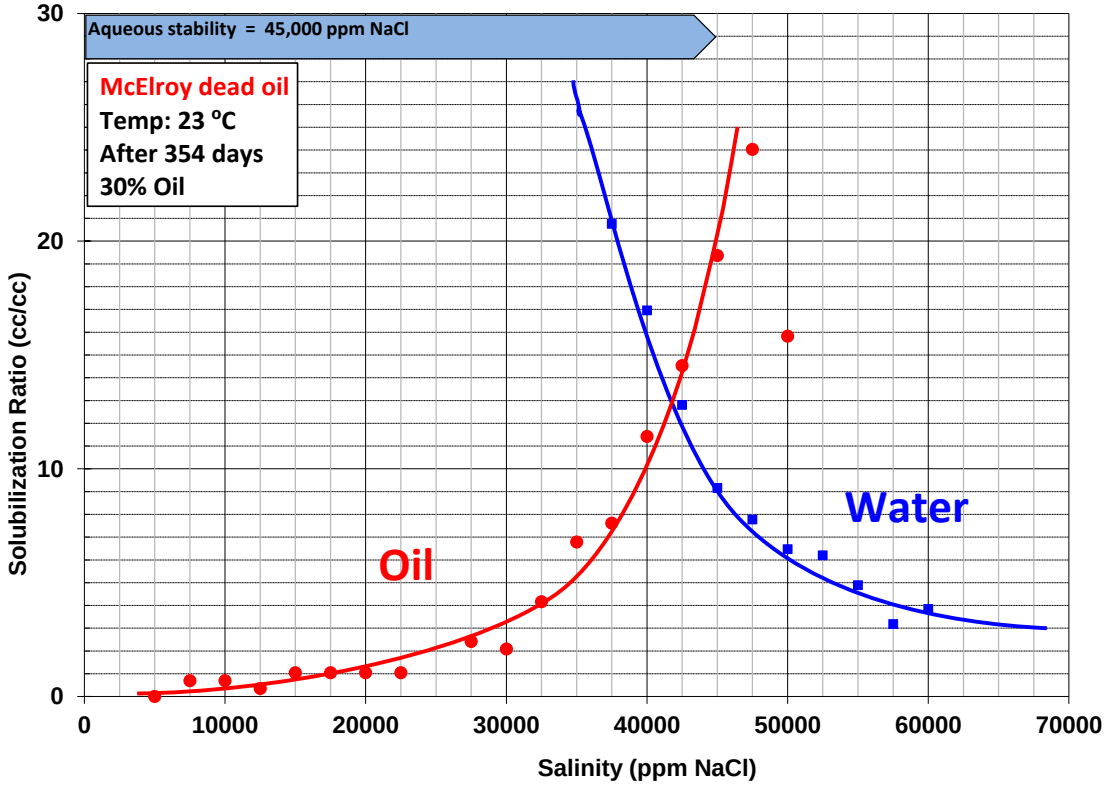


Figure 4.2: Solubilization ratios of oil and water for the 0.85 wt% C12-13-13PO-Sulfate, 0.15 wt% C15-18-IOS, and 1.0 wt% Phenol-1PO-2EO surfactant formulation. Based on where the curves cross, the optimal salinity was about 42,000 ppm NaCl.

Surfactant Formulations 3 to 6

Surfactant formulations 3 to 6 are variations of the surfactant formulation 2 in terms of surfactant and/or co-solvent concentrations.

Surfactant Formulation 7

The surfactant formulation is 0.3 wt% C20-24-IOS, 0.4 wt% Ole C18-35PO-10EO-Sulfate, 0.3 wt% 2-Ethylhexanol-7PO-Sulfate, and 1.0 wt% IBA-1PO-2EO. It formed a stable microemulsion with the McElroy dead oil at 23 ºC, the experimental temperature. A salinity scan was done by adding NaCl to deionized water and using 30% oil volume fraction. Figure 4.3 shows the solubilization ratios of oil and water at different salinities after 216 days of equilibration. The solubilization ratio at the optimal salinity of about 47,500 ppm NaCl was about 13. The IFT at the optimal salinity was estimated to be approximately $1.8x10^{-3}$ dynes/cm using the solubilization ratio of 13 in the Huh's equation (Huh 1979). The emulsion test indicated the lowest IFT was at 50,000 ppm NaCl. The aqueous surfactant solution was clear and stable up to 55,000 ppm NaCl for at least 216 days. The microemulsion viscosity at the optimal salinity was 21 cp at 23 ºC, about 1.7 times higher than the oil viscosity.

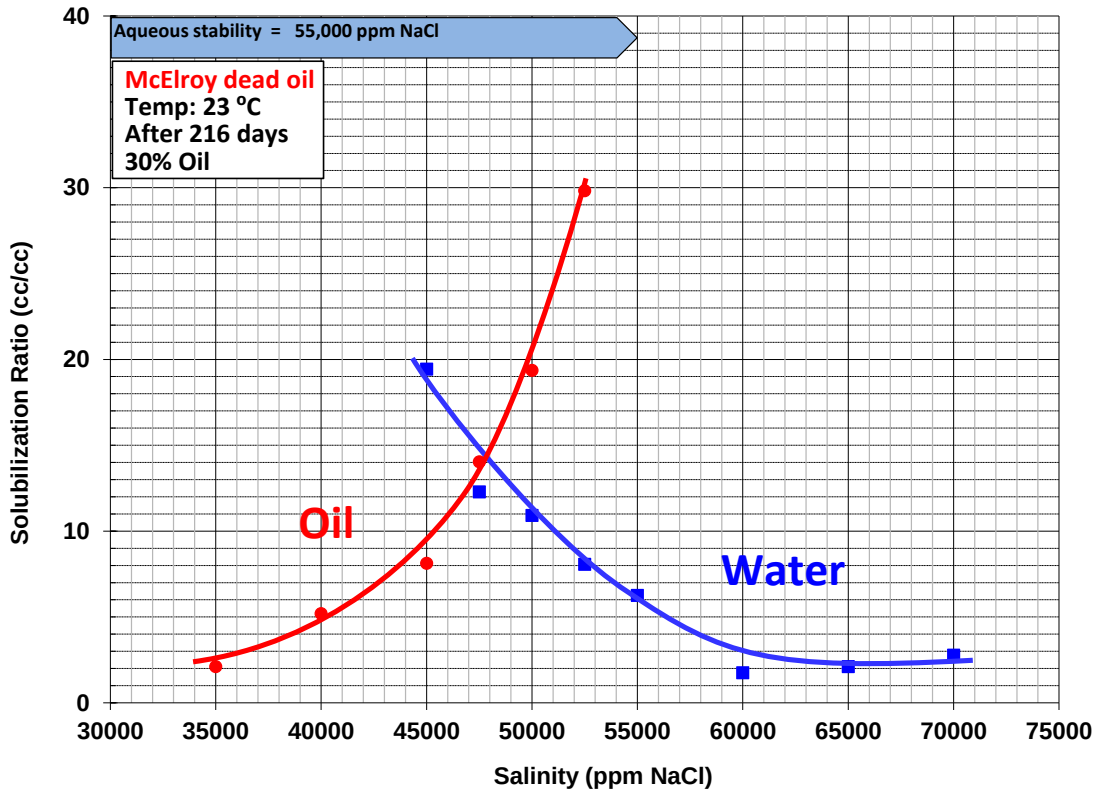


Figure 4.3: Solubilization ratios of oil and water for the 0.3 wt% C20-24-IOS, 0.4 wt% Ole C18-35PO-10EO-Sulfate, 0.3 wt% 2-Ethylhexanol-7PO-Sulfate, and 1.0 wt% IBA-1PO-2EO surfactant formulation. Based on where the curves cross, the optimal salinity was about 47,500 ppm NaCl.

Surfactant Formulation 8

The surfactant formulation is 0.5 wt% TDA-13PO-Sulfate, 0.5 wt% C20-24-IOS, and 0.5 wt% Phenol-1PO-5EO. It formed a stable microemulsion with the Oregon Basin surrogate oil at 45 °C, the experimental temperature. A salinity scan was done by adding Na2CO3 to a synthetic brine and using 30% oil volume fraction. Figure 4.4 shows the solubilization ratios of oil and water at different salinities after 106 days of equilibration. The solubilization ratio at the optimal salinity of about 42,000 ppm TDS was about 18. The IFT at the optimal salinity was estimated to be approximately 9.3×10^{-4} dynes/cm

using the solubilization ratio of 18 in the Huh's equation (Huh 1979). The emulsion test indicated the lowest IFT was at 43,000 ppm TDS. The aqueous surfactant solution was clear and stable up to 45,800 ppm TDS for at least 106 days. The microemulsion viscosity at the optimal salinity was 25 cp, about 3.6 times higher than the oil viscosity.

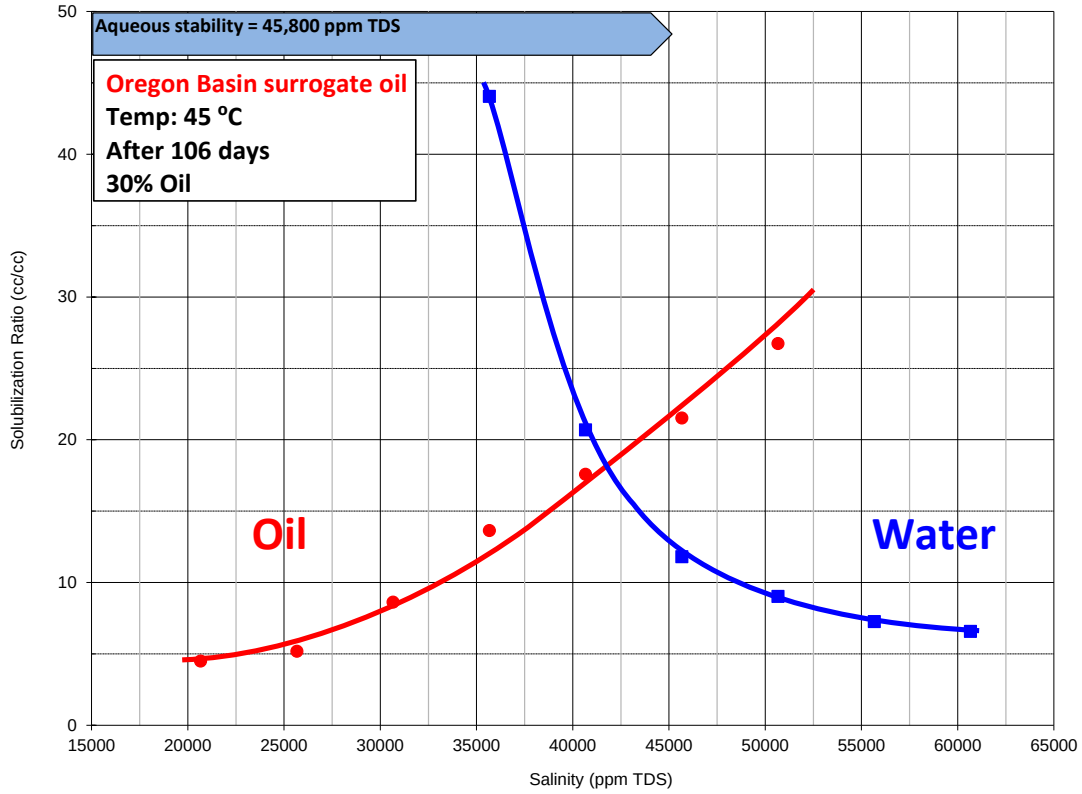


Figure 4.4: Solubilization ratios of oil and water for the 0.5 wt% TDA-13PO-Sulfate, 0.5 wt% C20-24-IOS, and 0.5 wt% Phenol-1PO-5EO surfactant formulation. Based on where the curves cross, the optimal salinity was about 42,000 ppm TDS.

Surfactant Formulation 9

The surfactant formulation is 0.1 wt% TDA-13PO-Sulfate, 0.2 wt% C20-24-IOS, 0.2 wt% TDA-45PO-10EO-Sulfate, and 0.25 wt% 2-Ethylhexanol-7PO-Sulfate. It formed a stable microemulsion with the RBD dead oil at 23 °C, the experimental

temperature. A salinity scan was done by adding Na2CO3 to a synthetic brine and using 30% oil volume fraction. Figure 4.5 shows the solubilization ratios of oil and water at different salinities after 111 days of equilibration. The solubilization ratio at the optimal salinity of about 57,500 ppm TDS was about 32. The IFT at the optimal salinity was estimated to be approximately 2.9×10^{-4} dynes/cm using the solubilization ratio of 32 in the Huh's equation (Huh 1979). The emulsion test indicated the lowest IFT was at 58,500 ppm TDS. The aqueous surfactant solution was clear and stable up to 63,400 ppm TDS for at least 111 days. The microemulsion viscosity at the optimal salinity was 20 cp, about 1.8 times higher than the oil viscosity.

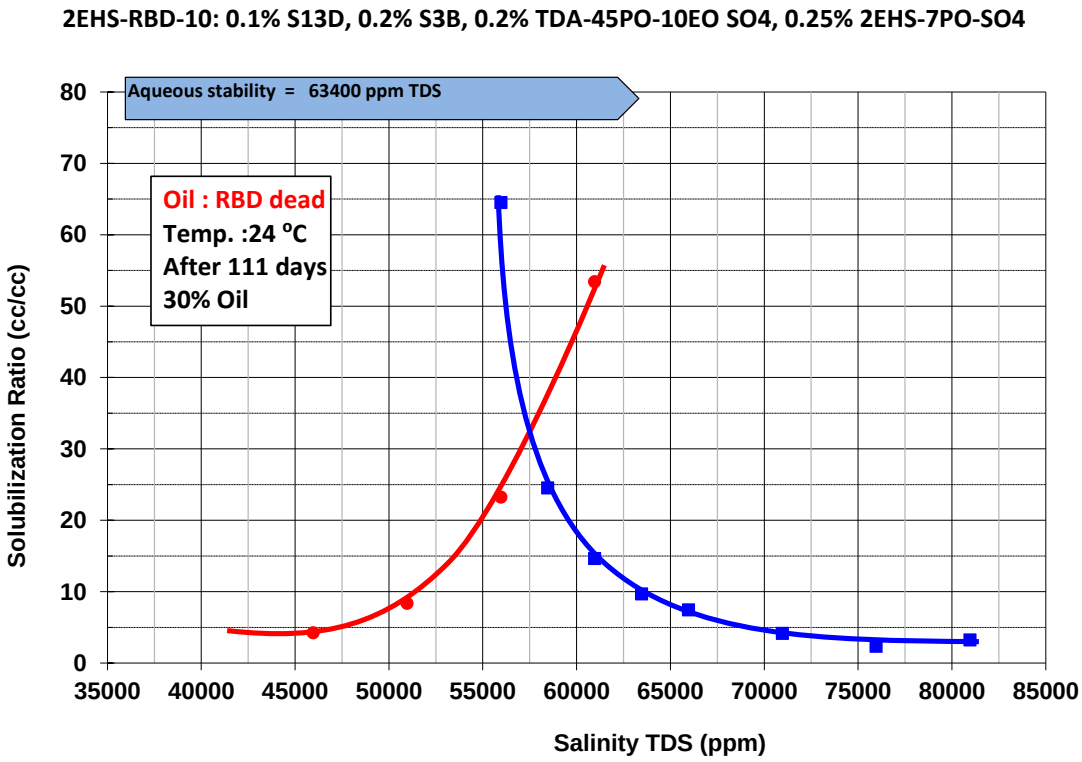


Figure 4.5: Solubilization ratios of oil and water for the 0.1 wt% TDA-13PO-Sulfate, 0.2 wt% C20-24-IOS, 0.2 wt% TDA-45PO-10EO-Sulfate, and 0.25 wt% 2-Ethylhexanol-7PO-Sulfate surfactant formulation. Based on where the curves cross, the optimal salinity was about 57,500 ppm TDS.

Surfactant Formulation 10

The surfactant formulation is 0.5 wt% C28-25PO-45EO-COO-, 0.2 wt% C15-18-IOS, 0.3 wt% C19-28-IOS, and 1 wt% EDTA. It formed a stable microemulsion with the SAMA surrogate oil at 78 °C, the experimental temperature. A salinity scan was done by adding NaCl to 30,000 ppm Na2CO3 brine and using 30% oil volume fraction. Figure 4.6 shows the solubilization ratios of oil and water at different salinities after 46 days of equilibration. The solubilization ratio at the optimal salinity of about 69,000 ppm TDS was about 9. The IFT at the optimal salinity was estimated to be approximately 3.7×10^{-3} dynes/cm using the solubilization ratio of 9 in the Huh's equation (Huh 1979). The emulsion test indicated the lowest IFT was at 80,000 ppm TDS. The aqueous surfactant solution was clear and stable up to 90,000 ppm TDS for at least 46 days. The microemulsion viscosity at the optimal salinity was 20 cp, about 2.9 times higher than the oil viscosity.

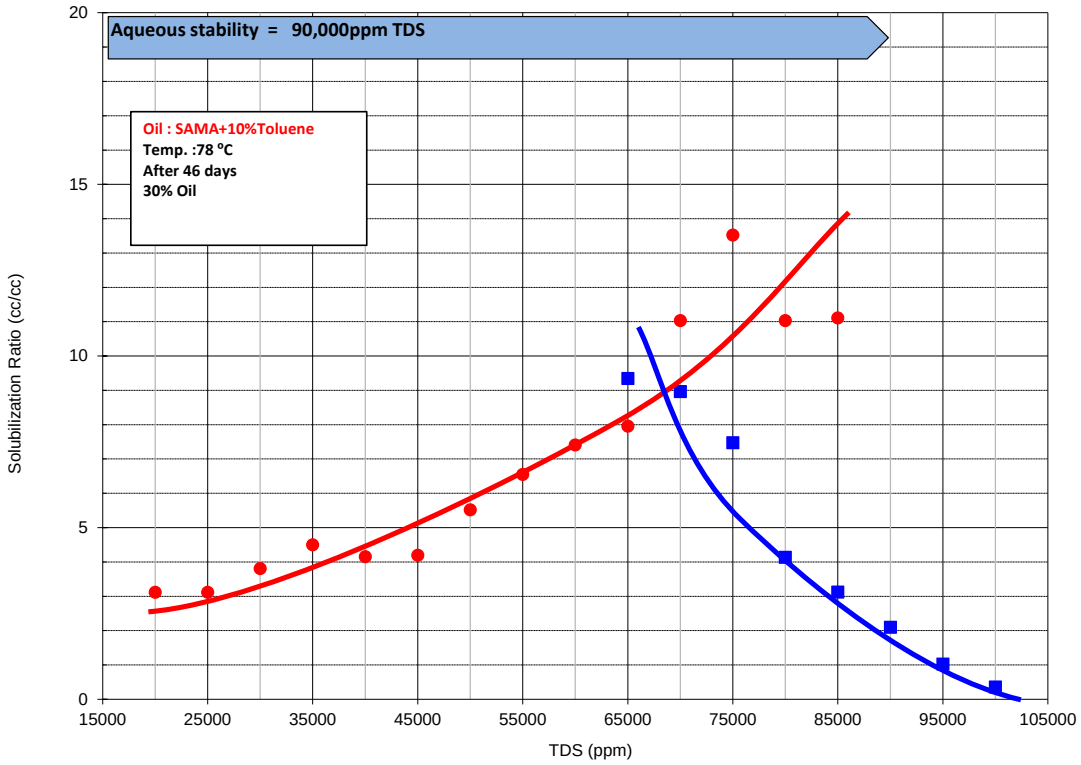


Figure 4.6: Solubilization ratios of oil and water for the 0.5 wt% C28-25PO-45EO-COO-, 0.2 wt% C15-18-IOS, 0.3 wt% C19-28-IOS, and 1 wt% EDTA surfactant formulation. Based on where the curves cross, the optimal salinity was about 69,000 ppm TDS.

Surfactant Formulation 11

The surfactant formulation is 0.5 wt% C28-25PO-45EO-COO-, 0.2 wt% C15-18-IOS, 0.3 wt% C19-28-IOS, and 0 wt% EDTA. It formed a stable microemulsion with the SAMA surrogate oil at 78 °C, the experimental temperature. A salinity scan was done by adding NaCl to 30,000 ppm Na2CO3 brine and using 30% oil volume fraction. Figure 4.7 shows the solubilization ratios of oil and water at different salinities after 46 days of equilibration. The solubilization ratio at the optimal salinity of about 67,000 ppm TDS was about 10. The IFT at the optimal salinity was estimated to be approximately 3.0×10^{-3}

dynes/cm using the solubilization ratio of 10 in the Huh's equation (Huh 1979). The emulsion test indicated the lowest IFT was at 75,000 ppm TDS. The aqueous surfactant solution was clear and stable up to 85,000 ppm TDS for at least 46 days. The microemulsion viscosity at the optimal salinity was 20 cp, about 2.9 times higher than the oil viscosity.

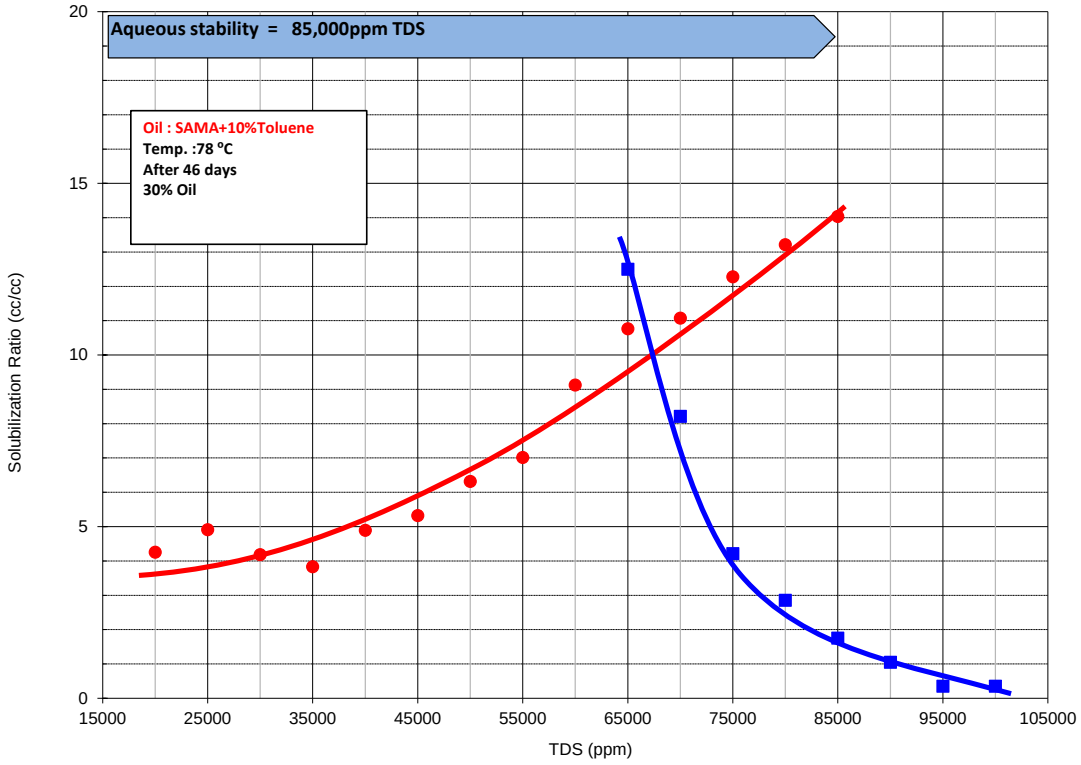


Figure 4.7: Solubilization ratios of oil and water for the 0.5 wt% C28-25PO-45EO-COO-, 0.2 wt% C15-18-IOS, 0.3 wt% C19-28-IOS, and 0 wt% EDTA surfactant formulation. Based on where the curves cross, the optimal salinity was about 67,000 ppm TDS.

4.2 Experimental Oil Recovery

This section presents the oil recovery results for the spontaneous imbibition experiments listed in Table 4.1. Oil recovery was shown as a percent of the original oil in

place (OOIP), defined as the volume of oil in the core before surfactant imbibition. The spontaneous imbibition experiments were conducted using the procedure described in section 3.4 Experimental Procedure. The experimental conditions are shown in Table 4.1. Many photographs of the imbibition cells and cores were taken during the experiments.

Experiment IE 21

A 3.76 cm diameter by 9.55 cm height (length) Texas cream limestone outcrop core was used for experiment IE 21. To prepare for imbibition, the core was initially fully vacuum-saturated with McElroy dead oil at 23 ºC. The core was then aged in McElroy oil at 75 ºC for 16 days. After preparation, the core was first immersed in 40,000 ppm NaCl brine inside the imbibition cell at 23 °C to observe oil recovery. After 7 minutes of brine imbibition, tiny oil droplets appeared on the side and top surfaces of the core as shown in Figure 4.8. The oil droplets grew in size after 24 hours of brine imbibition as shown in Figure 4.9. However, the droplets were always attached to the surfaces of the core and did not rise up to the air-brine interface. Figure 4.10 illustrates that the contact angle θ (measured through the denser brine phase) for a typical oil droplet on the top surface of the core was larger than 90º, which indicated that aging the core at 75 ºC for 16 days had rendered it oil wet.

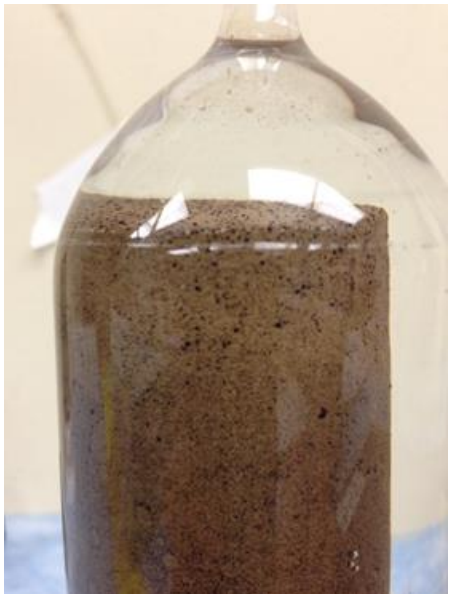


Figure 4.8: Tiny oil droplets on the surfaces of the core after 7 minutes of brine imbibition.

Figure 4.9: Large oil droplets on the surfaces of the core after 24 hours of brine imbibition.

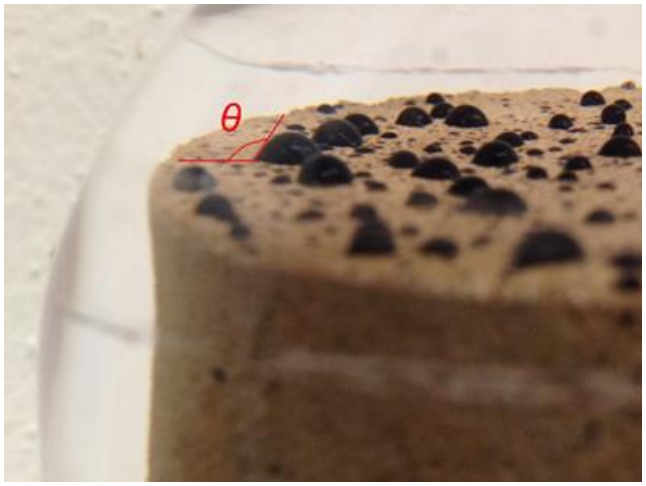


Figure 4.10: Contact angle θ larger than 90° indicated oil-wetness.

After brine imbibition, the core was immersed in an aqueous solution of 0.85 wt% C12-13-13PO-Sulfate, 0.15 wt% C15-18-IOS, and 1.0 wt% Phenol-1PO-2EO and at 23 ºC. The salinity of the surfactant solution was 40,000 ppm NaCl, which was the optimal salinity with NaCl. The oil was produced in the form of an emulsion, causing the color of the liquid surrounding the core to gradually change from clear to dark as shown in Figure 4.11. About 50 ml of fresh surfactant solution was flowed into the cell to flush out about 50 ml of the emulsion once per day to measure the oil content in the emulsion. About 105 PVs of fresh surfactant solution was injected over 64 days. During surfactant imbibition, no oil droplets or blobs with sizes large enough to detect with the naked eye appeared on the surfaces of the core. All of the produced oil was in the form of an emulsion.

Figure 4.11: Oil was produced as emulsion.

The oil recovery and oil saturation versus time are shown in Figure 4.12. The final oil recovery after 64 days was 58% OOIP and the final oil saturation was 0.42. Although oil was still being produced, the experiment was stopped to measure the permeability of the core. The brine permeability of the core was 7 md. The final oil recovery determined from weighing the core after 64 days of surfactant imbibition was 26% OOIP, which differs significantly from the value based on the emulsion density.

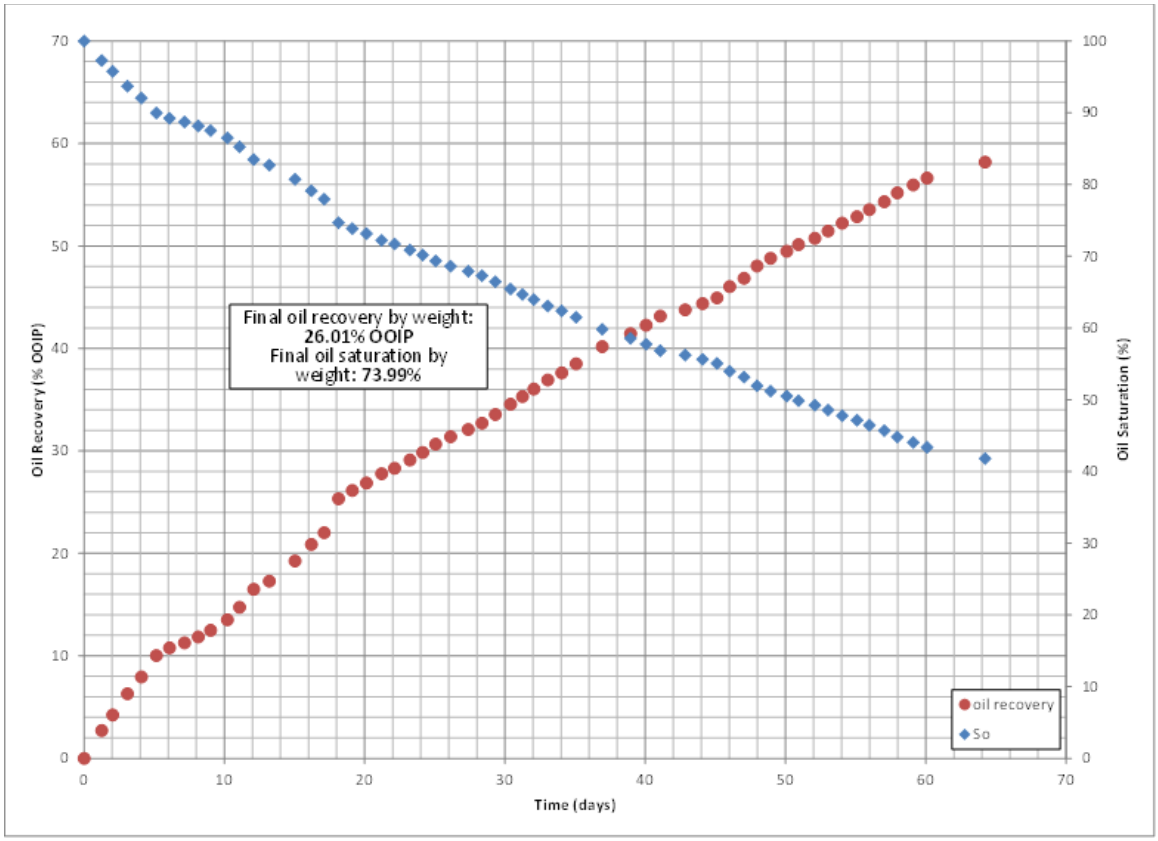


Figure 4.12: Experiment IE 21 oil recovery and oil saturation versus time.

Experiment IE 25

Experiment IE 25 was a duplicate experiment of IE 21. A 3.77 cm diameter by 9.78 cm height (length) Texas cream limestone outcrop core was used for experiment IE 25. To prepare for imbibition, the core was initially fully vacuum-saturated with McElroy dead oil at 23 ºC. The core was then aged in McElroy oil at 23 ºC for 34 days. After preparation, the core was first immersed in 40,000 ppm NaCl brine inside the imbibition cell at 23 °C to observe oil recovery. No oil was recovered after 22 hours, which indicated that aging the core at 23 ºC for 34 days had rendered it oil-wet. The core appeared to be more oil-wet after aging at a lower temperature and for a longer time compared to IE 21.

After brine imbibition, the core was immersed in an aqueous solution of 0.85 wt% C12-13-13PO-Sulfate, 0.15 wt% C15-18-IOS, and 1.0 wt% Phenol-1PO-2EO and at 23 ºC. The salinity of the surfactant solution was 40,000 ppm NaCl, which was the optimal salinity with NaCl. The oil was produced in the form of an emulsion, causing the color of the liquid surrounding the core to gradually change from clear to dark. At the beginning of the experiment, about 50 ml of fresh surfactant solution was flowed into the cell to flush out about 50 ml of the emulsion once per day to measure the oil content in the emulsion. After about 70 days of surfactant imbibition, about 50 ml of the emulsion was flushed out once per 4 days to measure the oil content. About 101 PVs of fresh surfactant solution was injected over 176 days. During surfactant imbibition, no oil droplets or blobs with sizes large enough to detect with the naked eye appeared on the surfaces of the core. All of the produced oil was in the form of emulsion.

The oil recovery and oil saturation versus time are shown in Figure 4.13. The final oil recovery after 176 days was 76% OOIP and the final oil saturation was 0.24. Although oil was still being produced, the experiment was stopped to measure the permeability of the core. The brine permeability of the core was 47 md. The final oil recovery determined from weighing the core after 176 days of surfactant imbibition was 81% OOIP, which is in good agreement with the value based on the emulsion density.

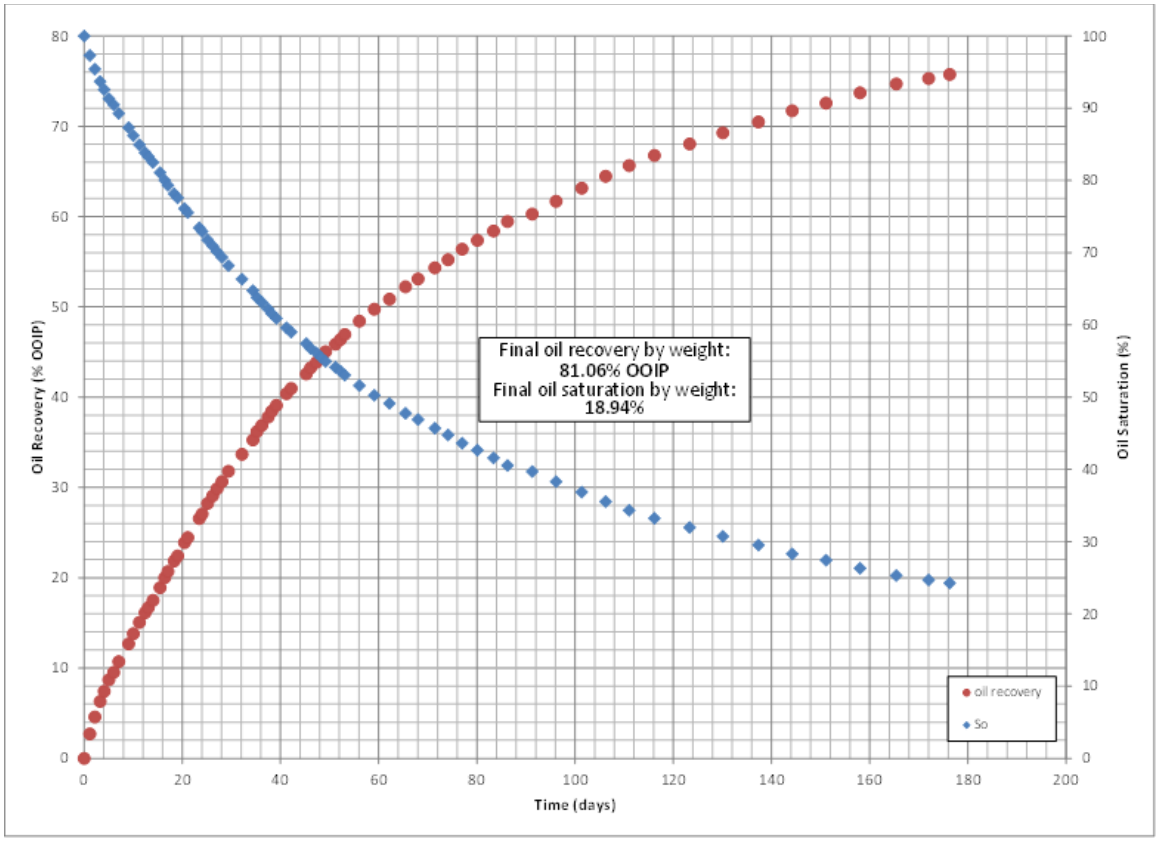


Figure 4.13: Experiment IE 25 oil recovery and oil saturation versus time.

Experiment IE 49

Experiment IE 49 was a duplicate experiment of IE 21 and 25. A 3.76 cm diameter by 9.83 cm height (length) Texas cream limestone outcrop core was used for experiment IE 49. To prepare for imbibition, the core was initially fully vacuum-saturated with McElroy dead oil at 23 ºC. The core was then aged in McElroy oil at 23 ºC for 76 days. After preparation, the core was first immersed in 40,000 ppm NaCl brine inside the imbibition cell at 23 °C to observe oil recovery. No oil was recovered after 36 hours, which indicated that aging the core at 23 ºC for 76 days had rendered it oil-wet.

After brine imbibition, the core was immersed in an aqueous solution of 0.85 wt% C12-13-13PO-Sulfate, 0.15 wt% C15-18-IOS, and 1.0 wt% Phenol-1PO-2EO and at 23

ºC. The salinity of the surfactant solution was 40,000 ppm NaCl, which was the optimal salinity with NaCl. The oil was produced in the form of an emulsion, causing the color of the liquid surrounding the core to gradually change from clear to dark. About 50 ml of fresh surfactant solution was flowed into the cell to flush out about 50 ml of the emulsion once each 2 to 5 days to measure the oil content in the emulsion. The emulsion was flushed out more frequently at the beginning of the experiment than at later times. About 41 PVs of fresh surfactant solution was injected over 79 days. During surfactant imbibition, no oil droplets or blobs with sizes large enough to detect with the naked eye appeared on the surfaces of the core. All of the produced oil was in the form of emulsion.

The oil recovery and oil saturation versus time are shown in Figure 4.14. The final oil recovery after 104 days was 36% OOIP and the final oil saturation was 0.64. Although oil was still being produced, the experiment was stopped to measure the permeability of the core. The brine permeability of the core was 8 md. The final oil recovery determined from weighing the core after 104 days of surfactant imbibition was 41% OOIP, which is in good agreement with the value based on the emulsion density.

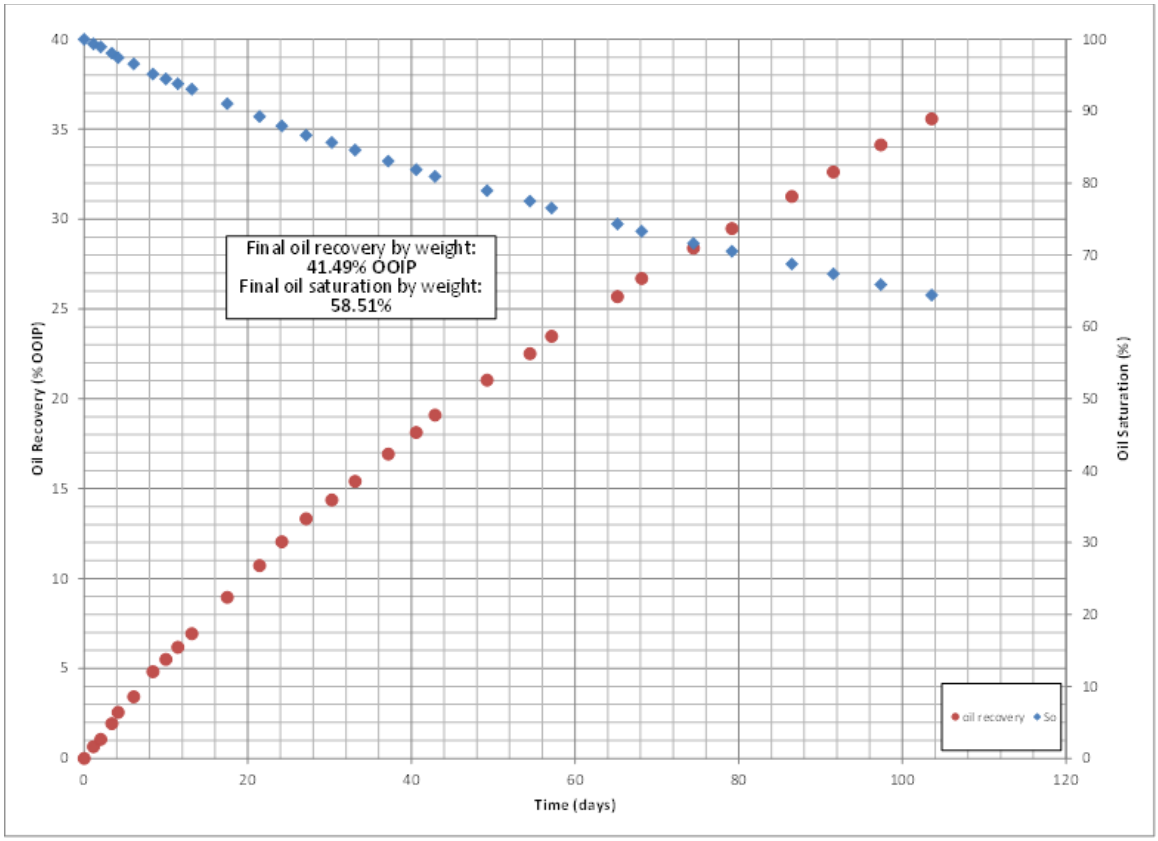


Figure 4.14: Experiment IE 49 oil recovery and oil saturation versus time.

Experiment IE 22

A 10.8 cm diameter by 9.43 cm height (length) Texas cream limestone outcrop core was used for experiment IE 22. To prepare for imbibition, the core was initially fully vacuum-saturated with McElroy dead oil at 23 ºC. The core was then aged in McElroy oil at 75 ºC for 17 days. After preparation, the core was first immersed in 40,000 ppm NaCl brine inside the imbibition cell at 23 °C to observe oil recovery. No oil was recovered after 24 hours, which indicated that aging the core at 75 ºC for 17 days had rendered it oil-wet. Figure 4.15 shows a photograph of the core after 24 hours of brine imbibition.

Figure 4.15: Experiment IE 22 did not produce any oil after 24 hours of brine imbibition.

After brine imbibition, the core was immersed in an aqueous solution of 0.85 wt% C12-13-13PO-Sulfate, 0.15 wt% C15-18-IOS, and 1.0 wt% Phenol-1PO-2EO and at 23 ºC. The salinity of the surfactant solution was 40,000 ppm NaCl, which was the optimal salinity with NaCl. The oil was produced in the form of an emulsion, causing the color of the liquid surrounding the core to gradually change from clear to dark as shown in Figure 4.16. About 100 ml of fresh surfactant solution was flowed into the cell to flush out about 100 ml of the emulsion once per day to measure the oil content in the emulsion. About 32 PVs of fresh surfactant solution was injected over 60 days. During surfactant imbibition, no oil droplets or blobs with sizes large enough to detect with the naked eye appeared on the surfaces of the core. All of the produced oil was in the form of emulsion.

Figure 4.16: Oil was produced as emulsion.

The oil recovery and oil saturation versus time are shown in Figure 4.17. The final oil recovery after 60 days was 24% OOIP and the final oil saturation was 0.76. Although oil was still being produced, the experiment was stopped to measure the permeability of the core. The brine permeability of the core was 7 md. The final oil recovery determined from weighing the core after 60 days of surfactant imbibition was 23% OOIP, which is in good agreement with the value based on the emulsion density.

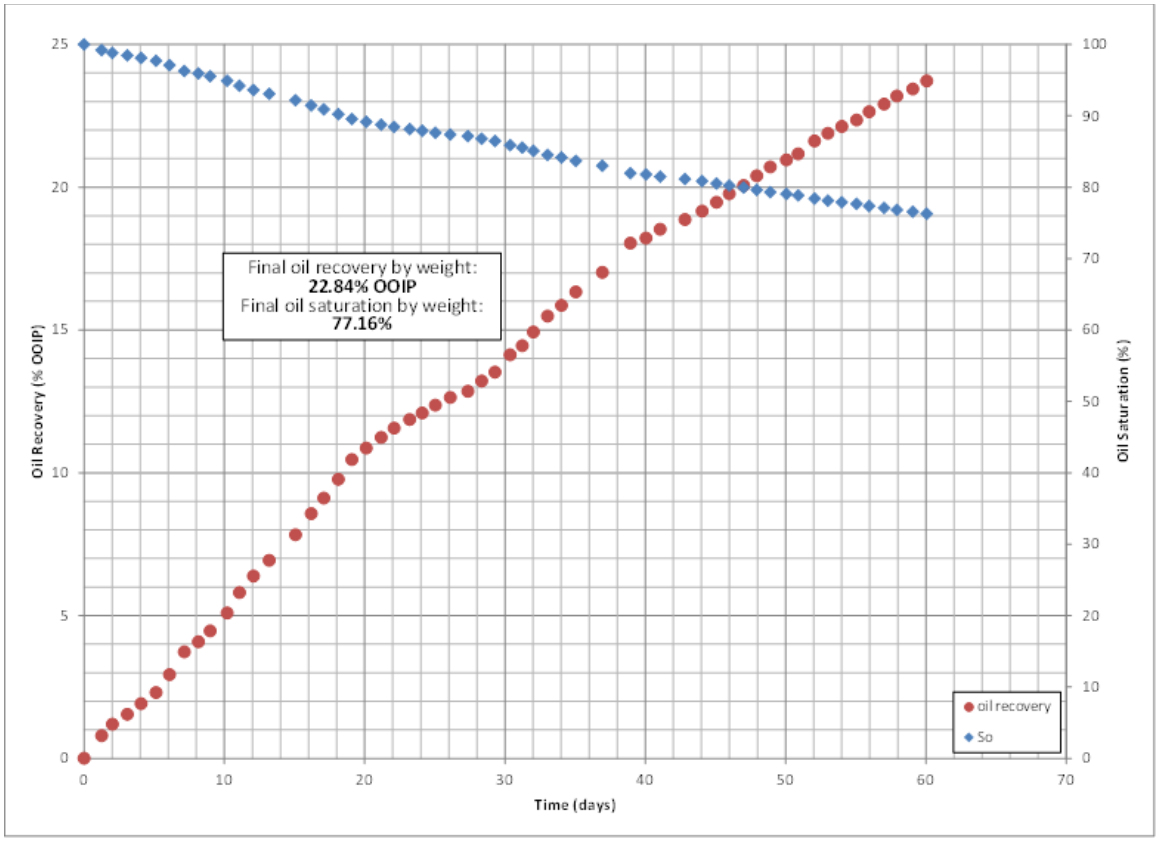


Figure 4.17: Experiment IE 22 oil recovery and oil saturation versus time.

Experiment IE 26

Experiment IE 26 was a duplicate experiment of IE 22. A 10.8 cm diameter by 9.35 cm height (length) Texas cream limestone outcrop core was used for experiment IE 26. To prepare for imbibition, the core was initially fully vacuum-saturated with McElroy dead oil at 23 ºC. The core was then aged in McElroy oil at 23 ºC for 6 days. After preparation, the core was first immersed in 40,000 ppm NaCl brine inside the imbibition cell at 23 °C to observe oil recovery. No oil was recovered after 23 hours, which indicated that aging the core at 23 ºC for 6 days had rendered it oil-wet. Aging the core at a lower temperature and for a shorter time compared to IE 22 yielded the same

wettability of the core before surfactant imbibition. Figure 4.18 shows a photograph of the core after 23 hours of brine imbibition.

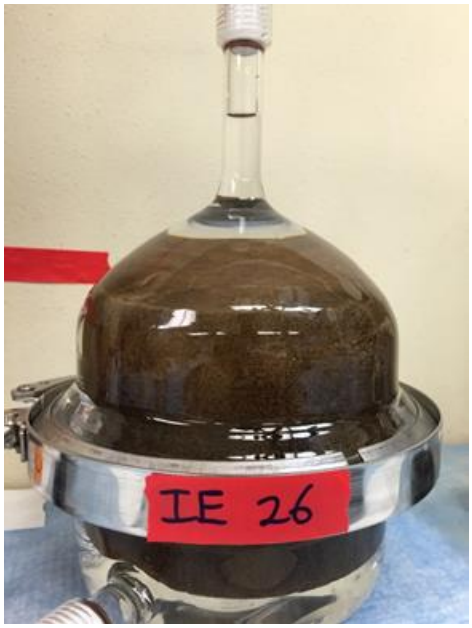


Figure 4.18: Experiment IE 26 did not produce any oil after 23 hours of brine imbibition.

After brine imbibition, the core was immersed in an aqueous solution of 0.85 wt% C12-13-13PO-Sulfate, 0.15 wt% C15-18-IOS, and 1.0 wt% Phenol-1PO-2EO and at 23 ºC. The salinity of the surfactant solution was 40,000 ppm NaCl, which was the optimal salinity with NaCl. The oil was produced in the form of an emulsion, causing the color of the liquid surrounding the core to gradually change from clear to dark. At the beginning of the experiment, about 100 ml of fresh surfactant solution was flowed into the cell to flush out about 100 ml of the emulsion once per day to measure the oil content in the emulsion. After about 130 days of surfactant imbibition, about 250 ml of the emulsion was flushed out once per week to measure the oil content. About 75 PVs of fresh surfactant solution was injected over 299 days. During surfactant imbibition, no oil

droplets or blobs with sizes large enough to detect with the naked eye appeared on the surfaces of the core. All of the produced oil was in the form of emulsion.

The oil recovery and oil saturation versus time are shown in Figure 4.19. The final oil recovery after 299 days was 54% OOIP and the final oil saturation was 0.46. Although oil was still being produced, the experiment was stopped to measure the permeability of the core. A 3.8 cm diameter by 9.4 cm height core was drilled from the center of the larger core to measure the permeability. The brine permeability of the core was 7 md. The final oil recovery determined from weighing the large intact core after 299 days of surfactant imbibition was 55% OOIP, which is in good agreement with the value based on the emulsion density.

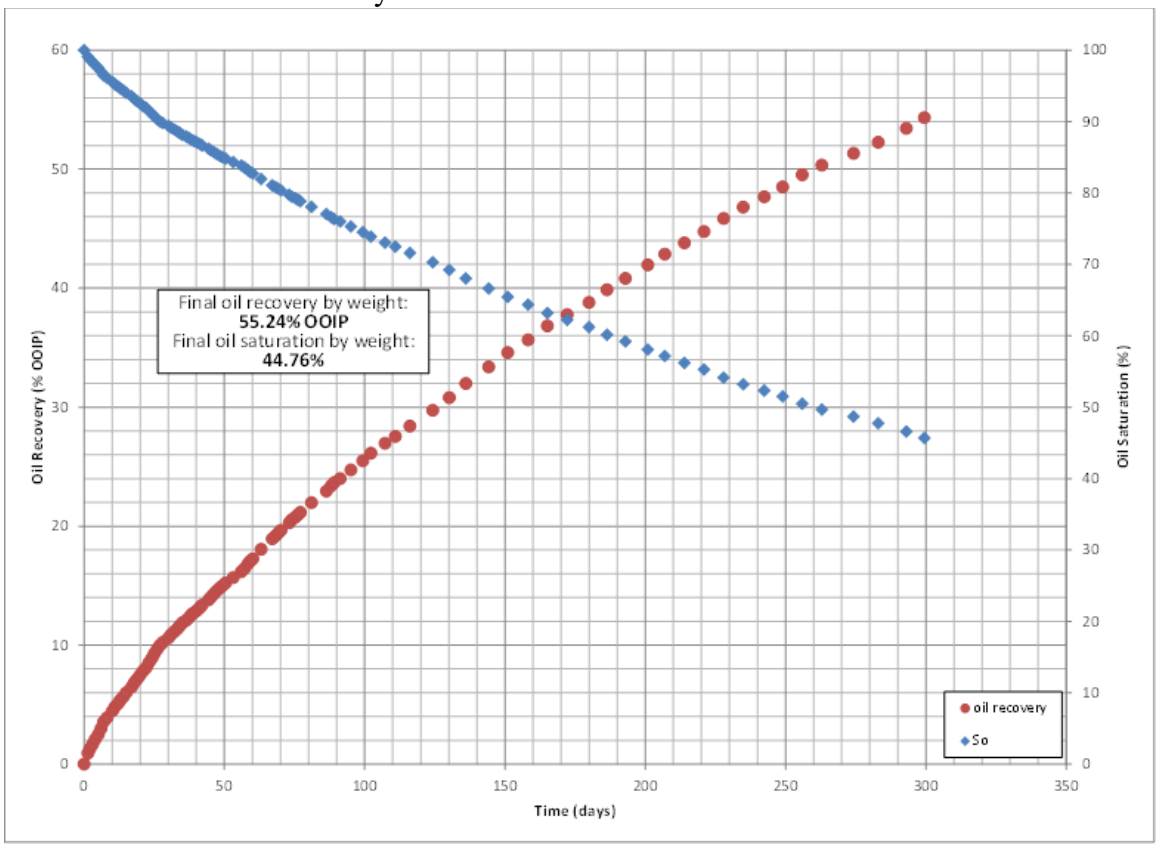


Figure 4.19: Experiment IE 26 oil recovery and oil saturation versus time.

Experiment IE 28

A rectangular Texas cream limestone outcrop core with a square base was used for experiment IE 28. The length of the side of the square base was 20.2 cm, and the height of the core was 9.50 cm. To prepare for imbibition, the core was initially fully vacuum-saturated with McElroy dead oil at 23 ºC. The core was then aged in McElroy oil at 23 ºC for 8 days. After preparation, the core was first immersed in 40,000 ppm NaCl brine inside the imbibition cell at 23 °C to observe oil recovery. No oil was recovered after 19 hours, which indicated that aging the core at 23 ºC for 8 days had rendered it oil-wet. Figure 4.20 shows photographs of the core after 19 hours of brine imbibition.

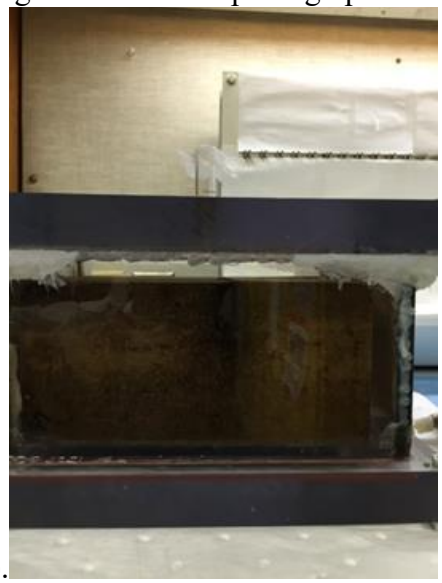
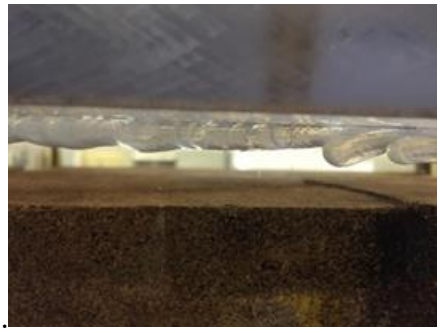
a).  b). 

Figure 4.20: a). Experiment IE 28 did not produce any oil after 19 hours of brine imbibition. b). Close-up photograph of the top surface of the core.

After brine imbibition, the core was immersed in an aqueous solution of 0.85 wt% C12-13-13PO-Sulfate, 0.15 wt% C15-18-IOS, and 1.0 wt% Phenol-1PO-2EO and at 23 ºC. The salinity of the surfactant solution was 40,000 ppm NaCl, which was the optimal salinity with NaCl. The oil was produced in the form of an emulsion, causing the color of

the liquid surrounding the core to gradually change from clear to dark as shown in Figure 4.21. At the beginning of the experiment, about 250 ml of fresh surfactant solution was flowed into the cell to flush out about 250 ml of the emulsion once per day to measure the oil content in the emulsion. After about 110 days of surfactant imbibition, about 250 ml of the emulsion was flushed out once every two or three days to measure the oil content. About 41 PVs of fresh surfactant solution was injected over 310 days. During surfactant imbibition, no oil droplets or blobs with sizes large enough to detect with the naked eye appeared on the surfaces of the core. All of the produced oil was in the form of emulsion.

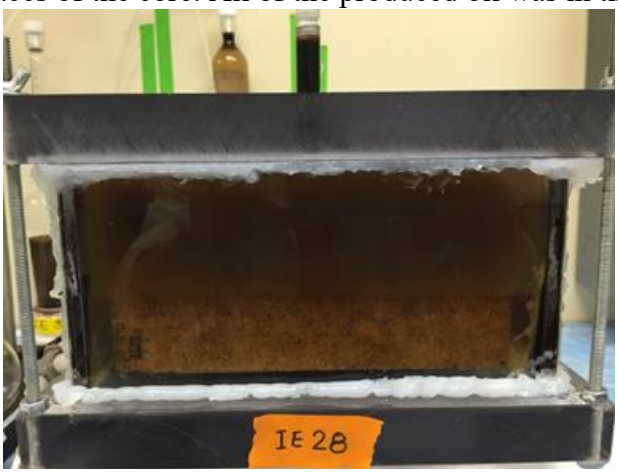


Figure 4.21: Oil was produced as emulsion.

The oil recovery and oil saturation versus time are shown in Figure 4.22. The final oil recovery after 369 days was 51% OOIP and the final oil saturation was 0.49. After 369 days, the experiment was stopped to examine the distribution of oil and water inside the core during surfactant imbibition by cleaving the core vertically into four smaller, equal-sized cubes as shown in Figure 4.23. The imbibition profiles are shown in Figure 4.24. The imbibition appeared to occur from the bottom and the sides of the core where the oil appeared to flow mainly in an upward direction along the imbibition front. The flow seemed to be predominantly co-current and governed by gravity forces. Two 1.5

inch diameter by 4 inch height cores were drilled vertically and horizontally from the small cubes to measure the permeability (Figure 4.23). The brine permeability of the vertically and horizontally drilled cores were 1 and 26 md respectively. The final oil recovery determined from weighing the large intact core after 369 days of surfactant imbibition was 55% OOIP, which is in good agreement with the value based on the emulsion density.

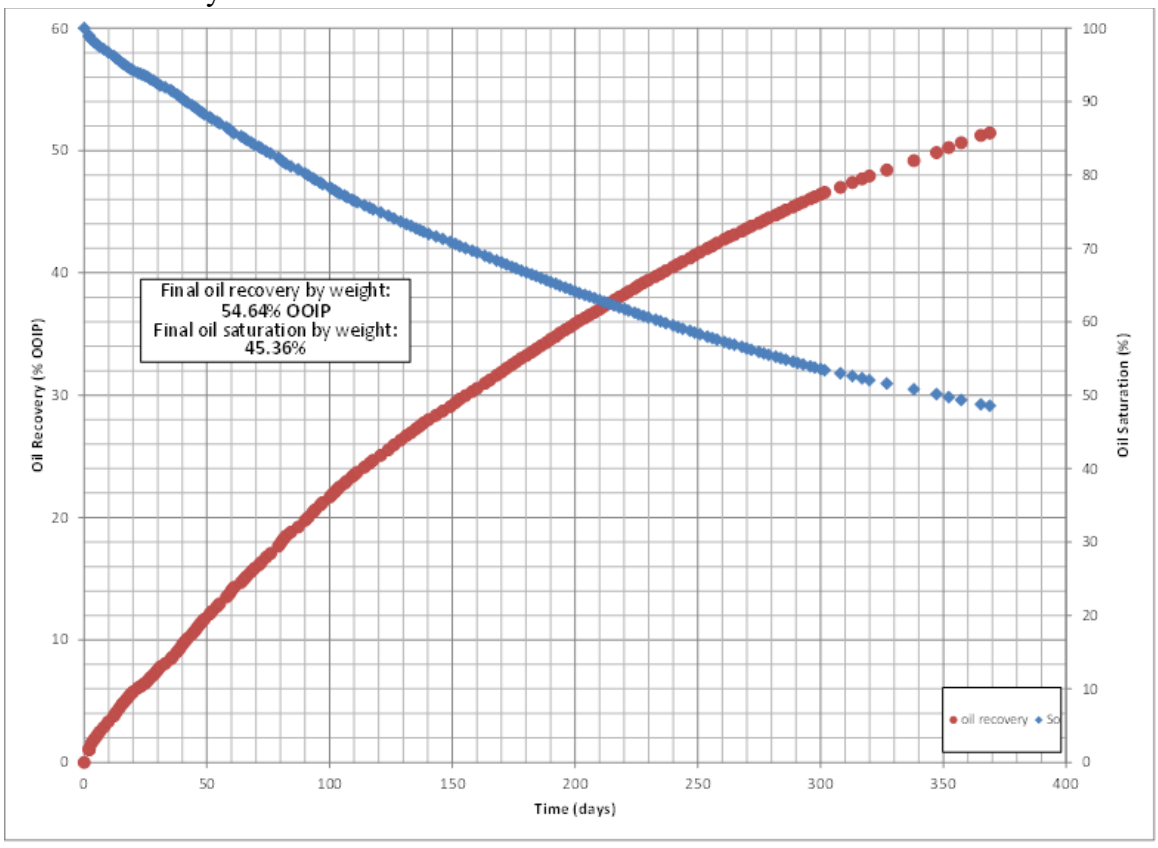


Figure 4.22: Experiment IE 28 oil recovery and oil saturation versus time.

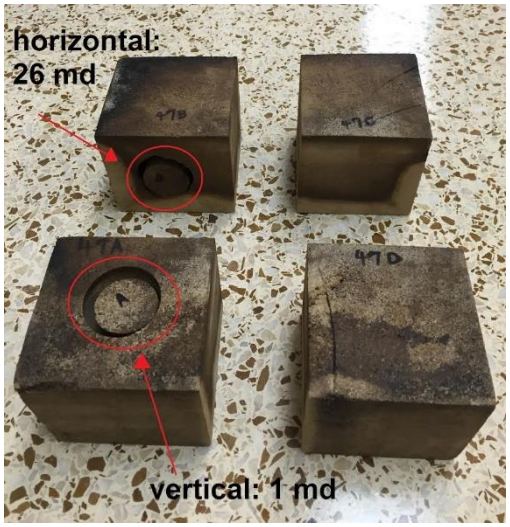


Figure 4.23: The large rectangular core was cleaved vertically into four smaller, equal-sized cubes to examine the imbibition profile. Two small cores were drilled from the cubes to measure the permeability.

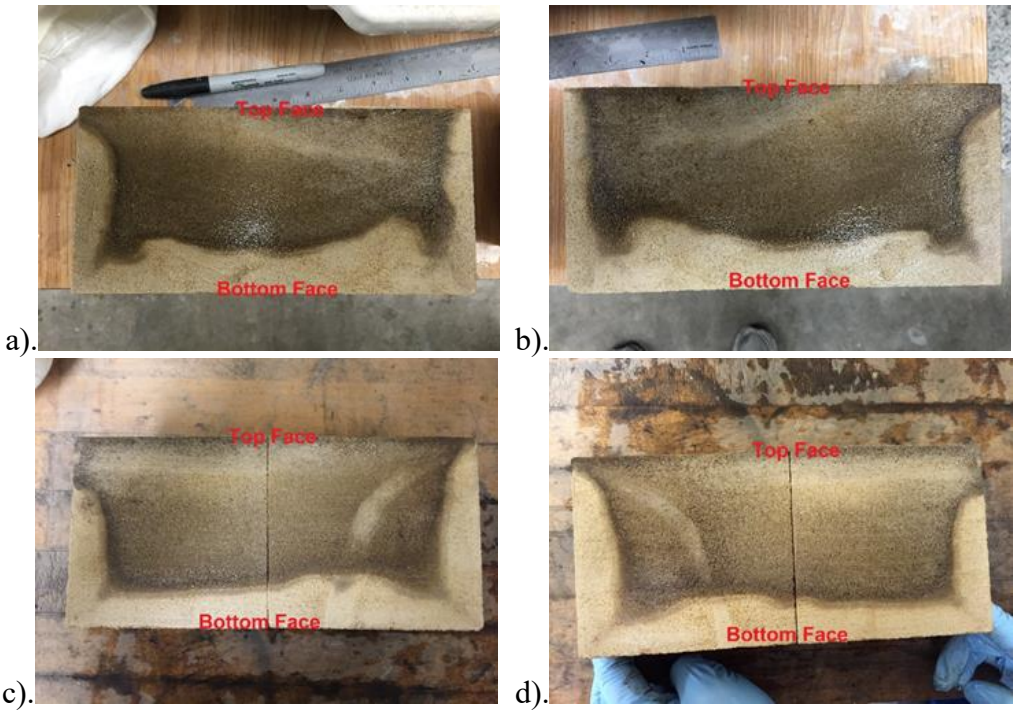


Figure 4.24: a-d). Imbibition profiles observed after cleaving the core vertically.

Experiment IE 29

A 3.77 cm diameter by 29.60 cm height (length) Texas cream limestone outcrop core was used for experiment IE 29. To prepare for imbibition, the core was initially fully vacuum-saturated with McElroy dead oil at 23 ºC. The core was then aged in McElroy oil at 75 ºC for 7 days. After preparation, the core was first immersed in 40,000 ppm NaCl brine inside the imbibition cell at 23 °C to observe oil recovery. Several oil droplets appeared on the top surface of the core after 20 hours as shown in Figure 4.25, but they did not rise up to the air-brine interface.

Figure 4.25: Several oil droplets on the top surface of the core after 20 hours of brine imbibition.

After brine imbibition, the core was immersed in an aqueous solution of 0.85 wt% C12-13-13PO-Sulfate, 0.15 wt% C15-18-IOS, and 1.0 wt% Phenol-1PO-2EO and at 23 ºC. The salinity of the surfactant solution was 40,000 ppm NaCl, which was the optimal salinity with NaCl. The oil was produced in the form of an emulsion, causing the color of the liquid surrounding the core to gradually change from clear to dark as shown in Figure

4.26. At the beginning of the experiment, about 100 ml of fresh surfactant solution was flowed into the cell to flush out about 100 ml of the emulsion once per day to measure the oil content in the emulsion. After about 30 days of surfactant imbibition, about 50 ml of the emulsion was flushed out once each 2 to 7 days to measure the oil content. About 80 PVs of fresh surfactant solution was injected over 304 days. During surfactant imbibition, no oil droplets or blobs with sizes large enough to detect with the naked eye appeared on the surfaces of the core. All of the produced oil was in the form of emulsion.

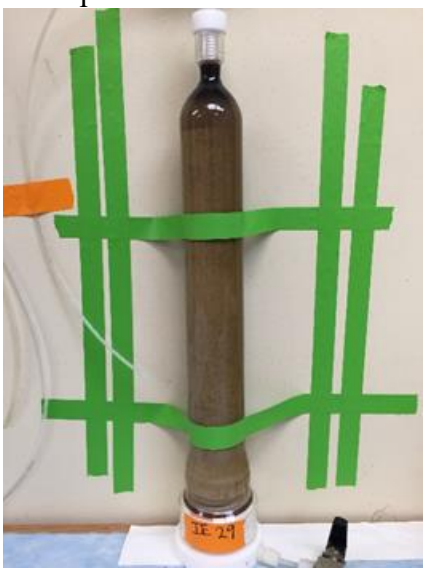


Figure 4.26: Oil was produced as emulsion.

The oil recovery and oil saturation versus time are shown in Figure 4.27. The final oil recovery after 304 days was 62% OOIP and the final oil saturation was 0.38. Although oil was still being produced, the experiment was stopped to measure the permeability of the core. The brine permeability of the core was 21 md. The final oil recovery determined from weighing the core after 304 days of surfactant imbibition was 67% OOIP, which is in good agreement with the value based on the emulsion density.

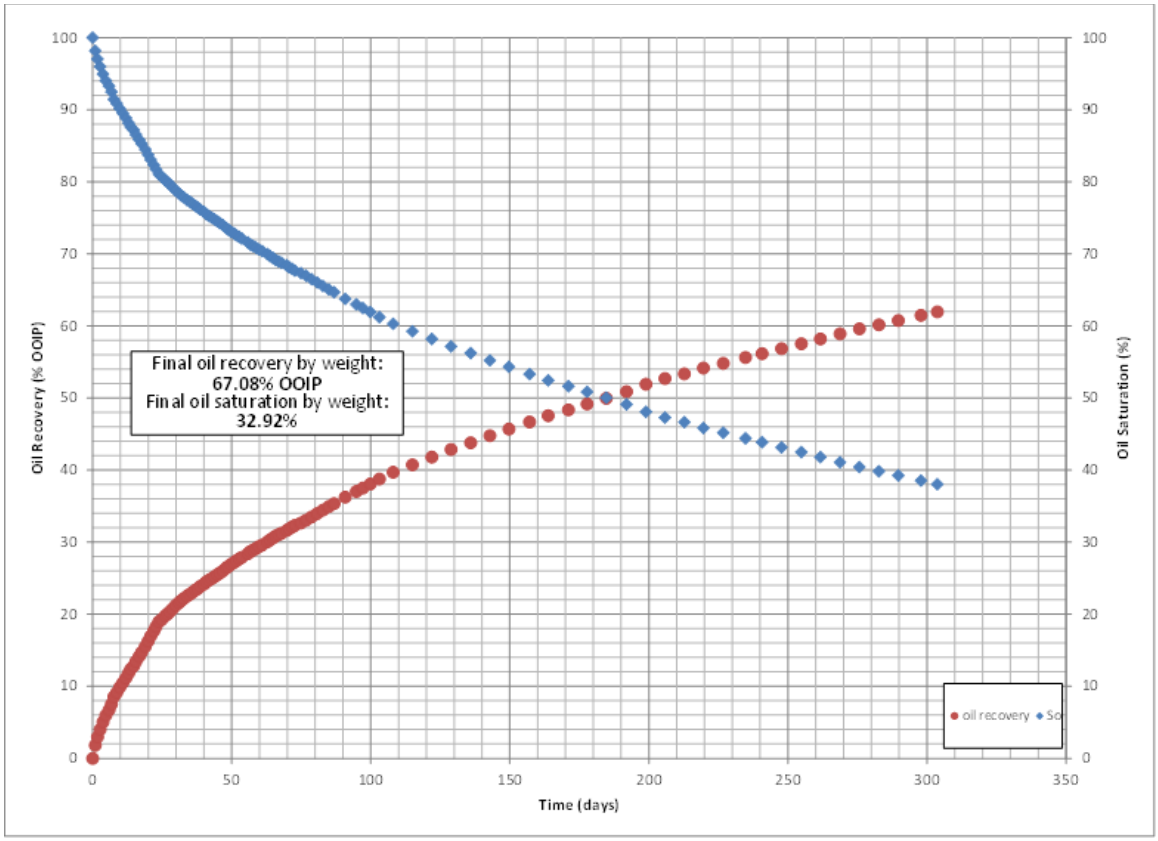


Figure 4.27: Experiment IE 29 oil recovery and oil saturation versus time.

Experiment IE 45

Experiment IE 45 was a duplicate experiment of IE 29. A 3.76 cm diameter by 29.40 cm height (length) Texas cream limestone outcrop core was used for experiment IE 45. To prepare for imbibition, the core was initially fully vacuum-saturated with McElroy dead oil at 23 ºC. The core was then aged in McElroy oil at 23 ºC for 6 days. After preparation, the core was first immersed in 40,000 ppm NaCl brine inside the imbibition cell at 23 °C to observe oil recovery. No oil was recovered after 49 hours, which indicated that aging the core at 23 ºC for 6 days had rendered it oil-wet.

After brine imbibition, the core was immersed in an aqueous solution of 0.85 wt% C12-13-13PO-Sulfate, 0.15 wt% C15-18-IOS, and 1.0 wt% Phenol-1PO-2EO and at 23

ºC. The salinity of the surfactant solution was 40,000 ppm NaCl, which was the optimal salinity with NaCl. The oil was produced in the form of an emulsion, causing the color of the liquid surrounding the core to gradually change from clear to dark. At the beginning of the experiment, about 100 ml of fresh surfactant solution was flowed into the cell to flush out about 100 ml of the emulsion once per day to measure the oil content in the emulsion. After about 10 days of surfactant imbibition, about 50 ml of the emulsion was flushed out once each 2 to 7 days to measure the oil content. About 50 PVs of fresh surfactant solution was injected over 264 days. During surfactant imbibition, no oil droplets or blobs with sizes large enough to detect with the naked eye appeared on the surfaces of the core. All of the produced oil was in the form of emulsion.

The oil recovery and oil saturation versus time are shown in Figure 4.28. The final oil recovery after 264 days was 40% OOIP and the final oil saturation was 0.60. Although oil was still being produced, the experiment was stopped to measure the permeability of the core. The brine permeability of the core was 10 md. The final oil recovery determined from weighing the core after 264 days of surfactant imbibition was 50% OOIP, which is in good agreement with the value based on the emulsion density.

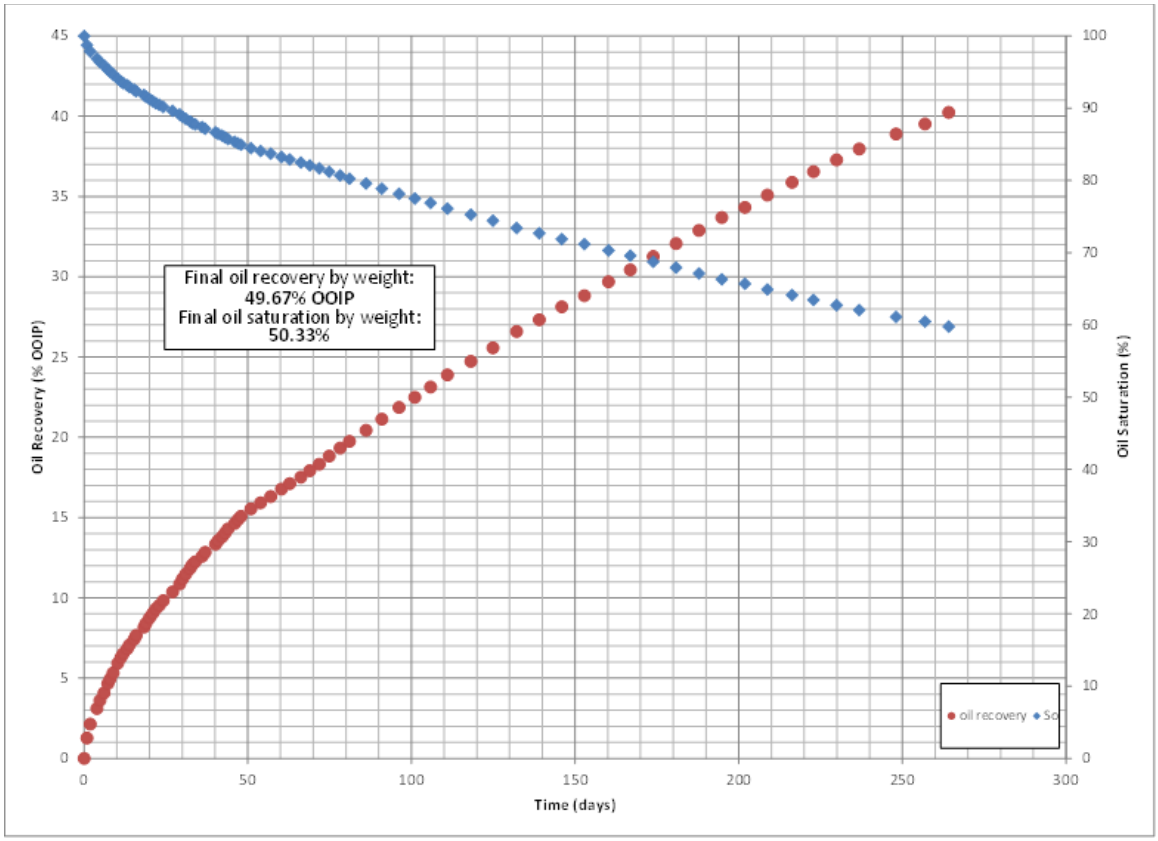


Figure 4.28: Experiment IE 45 oil recovery and oil saturation versus time.

Experiment IE 47

A 9.80 cm diameter by 29.23 cm height (length) Texas cream limestone outcrop core was used for experiment IE 47. To prepare for imbibition, the core was initially fully vacuum-saturated with McElroy dead oil at 23 ºC. The core was then aged in McElroy oil at 23 ºC for 6 days. After preparation, the core was first immersed in 40,000 ppm NaCl brine inside the imbibition cell at 23 °C to observe oil recovery. No oil was recovered after 25 hours, which indicated that aging the core at 23 ºC for 6 days had rendered it oil-wet. Figure 4.29 shows a photograph of the core after 25 hours of brine imbibition.

Figure 4.29: Experiment IE 47 did not produce any oil after 25 hours of brine imbibition.

After brine imbibition, the core was immersed in an aqueous solution of 0.85 wt% C12-13-13PO-Sulfate, 0.15 wt% C15-18-IOS, and 1.0 wt% Phenol-1PO-2EO and at 23 ºC. The salinity of the surfactant solution was 40,000 ppm NaCl, which was the optimal salinity with NaCl. The oil was produced in the form of an emulsion, causing the color of the liquid surrounding the core to gradually change from clear to dark. After about 28 days of surfactant imbibition, an opaque and cloudy middle phase formed within the fluids inside the imbibition cell as shown in Figure 4.30. The phase persisted for about 18 days. About 250 ml of fresh surfactant solution was flowed into the cell to flush out about 250 ml of the emulsion once each 2 to 3 days to measure the oil content in the emulsion. About 40 PVs of fresh surfactant solution was injected over 204 days. During surfactant imbibition, no oil droplets or blobs with sizes large enough to detect with the naked eye appeared on the surfaces of the core. All of the produced oil was in the form of emulsion.

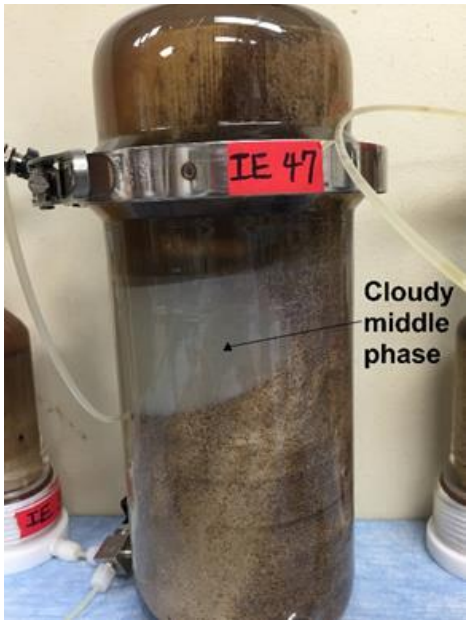


Figure 4.30: A cloudy middle phase was observed after about 28 days of surfactant imbibition.

The oil recovery and oil saturation versus time are shown in Figure 4.31. The final oil recovery after 204 days was 38% OOIP and the final oil saturation was 0.62. Although oil was still being produced, the experiment was stopped to measure the permeability of the core. A 3.8 cm diameter by 29.2 height core was drilled from the center of the larger core to measure the permeability. The brine permeability of the core was 11 md. The final oil recovery determined from weighing the large intact core after 204 days of surfactant imbibition was 93% OOIP, which differs significantly from the value based on the emulsion density. Figure 4.32 shows photographs of the core after completing the surfactant imbibition process. By examining the oil saturation on the surfaces of the core, the oil recovery of 93% OOIP obtained from weighing the core appeared to be inaccurate.

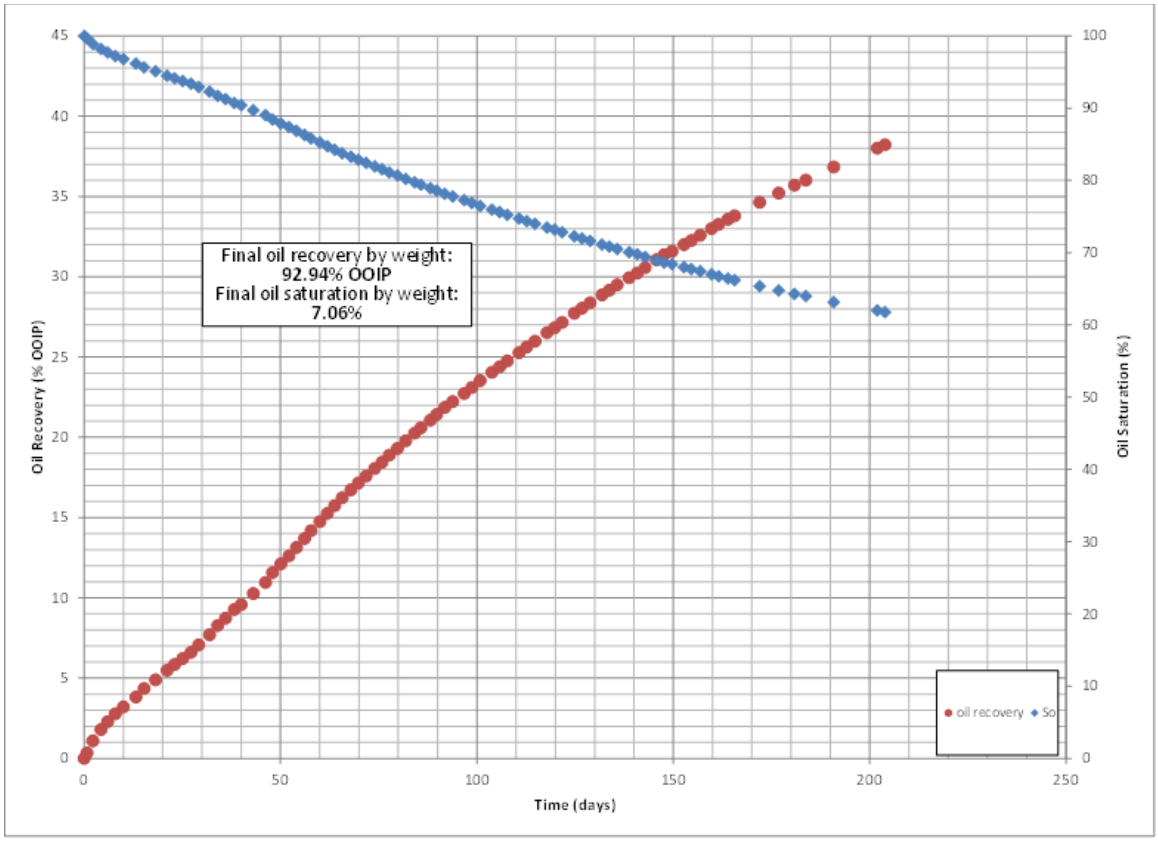


Figure 4.31: Experiment IE 47 oil recovery and oil saturation versus time.

Figure 4.32: Photographs of the core after completing the surfactant imbibition process.

Experiment IE 31

A 3.77 cm diameter by 9.26 cm height (length) Texas cream limestone outcrop core was used for experiment IE 31. To prepare for imbibition, the core was initially fully vacuum-saturated with McElroy dead oil at 23 ºC. The core was then aged in McElroy oil at 23 ºC for 30 days. After preparation, the core was first immersed in 50,000 ppm NaCl brine inside the imbibition cell at 23 °C to observe oil recovery. After 24 hours of brine imbibition, three small oil droplets appeared on the top surface of the core as shown in Figure 4.33. The oil droplets were always attached to the top surface of the core and did not rise up to the air-brine interface.

Figure 4.33: Three small oil droplets on the top surface of the core after 24 hours of brine imbibition.

After brine imbibition, the core was immersed in an aqueous solution of 0.3 wt% C20-24-IOS, 0.4 wt% Ole C18-35PO-10EO-Sulfate, 0.3 wt% 2-Ethylhexanol-7PO-Sulfate, and 1.0 wt% IBA-1PO-2EO and at 23 ºC. The salinity of the surfactant solution was 50,000 ppm NaCl, which was the optimal salinity with NaCl. The oil was produced

in the form of an emulsion, causing the color of the liquid surrounding the core to gradually change from clear to dark. At the beginning of the experiment, about 50 ml of fresh surfactant solution was flowed into the cell to flush out about 50 ml of the emulsion once per day to measure the oil content in the emulsion. After about 47 days of surfactant imbibition, about 50 ml of the emulsion was flushed out once each 2 to 7 days to measure the oil content. About 165 PVs of fresh surfactant solution was injected over 306 days. During surfactant imbibition, no oil droplets or blobs with sizes large enough to detect with the naked eye appeared on the surfaces of the core. All of the produced oil was in the form of emulsion.

The oil recovery and oil saturation versus time are shown in Figure 4.34. The final oil recovery after 306 days was 82% OOIP and the final oil saturation was 0.18. Although oil was still being produced, the experiment was stopped to measure the permeability of the core. The brine permeability of the core was 8 md. The final oil recovery determined from weighing the core after 306 days of surfactant imbibition was 57% OOIP, which differs significantly from the value based on the emulsion density.

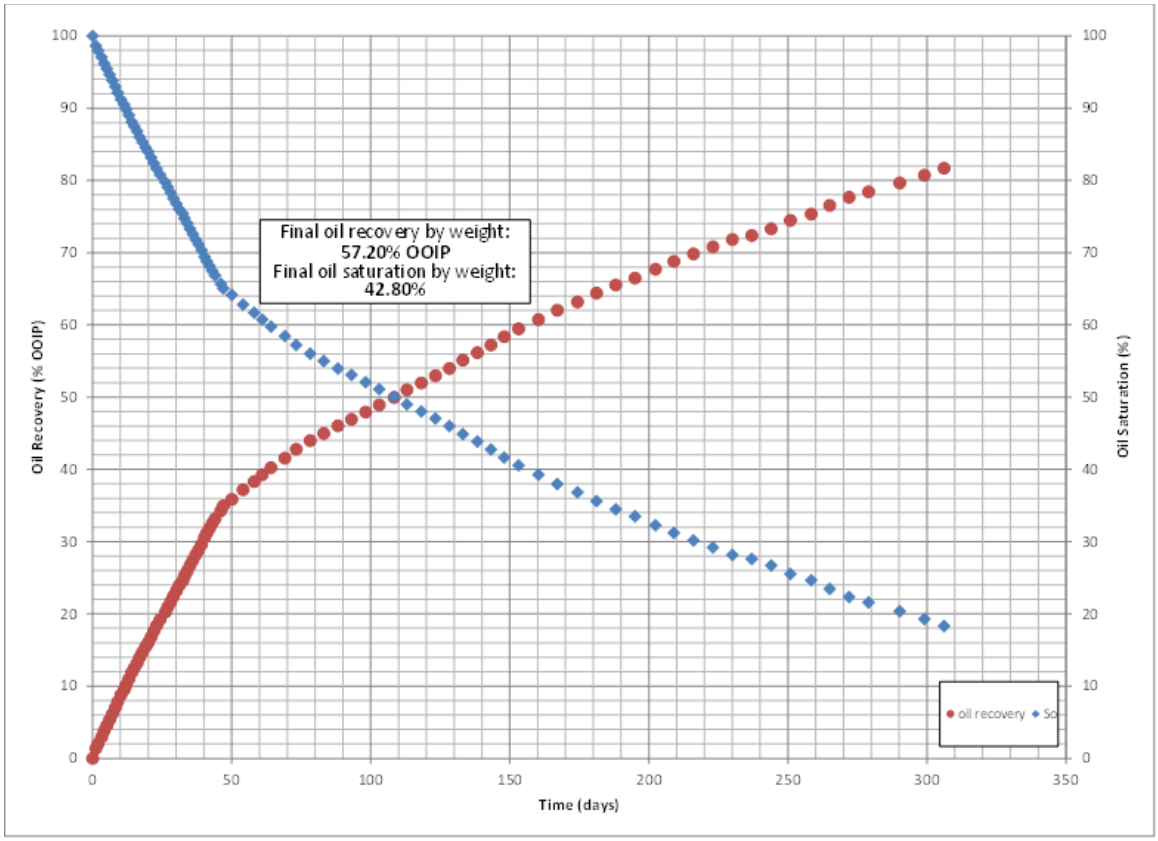


Figure 4.34: Experiment IE 31 oil recovery and oil saturation versus time.

Experiment IE 34

Experiment IE 34 was a duplicate experiment of IE 31. A 3.79 cm diameter by 10.01 cm height (length) Texas cream limestone outcrop core was used for experiment IE 34. To prepare for imbibition, the core was initially fully vacuum-saturated with McElroy dead oil at 23 ºC. The core was then aged in McElroy oil at 23 ºC for 12 days. After preparation, the core was first immersed in 50,000 ppm NaCl brine inside the imbibition cell at 23 °C to observe oil recovery. No oil was recovered after 48 hours, which indicated that aging the core at 23 ºC for 12 days had rendered it oil-wet. Figure 4.35 shows a photograph of the core after 48 hours of brine imbibition.

Figure 4.35: Experiment IE 34 did not produce any oil after 48 hours of brine imbibition.

After brine imbibition, the core was immersed in an aqueous solution of 0.3 wt% C20-24-IOS, 0.4 wt% Ole C18-35PO-10EO-Sulfate, 0.3 wt% 2-Ethylhexanol-7PO-Sulfate, and 1.0 wt% IBA-1PO-2EO and at 23 ºC. The salinity of the surfactant solution was 50,000 ppm NaCl, which was the optimal salinity with NaCl. The oil was produced in the form of an emulsion, causing the color of the liquid surrounding the core to gradually change from clear to dark. About 50 ml of fresh surfactant solution was flowed into the cell to flush out about 50 ml of the emulsion once each 3 to 7 days to measure the oil content in the emulsion. About 111 PVs of fresh surfactant solution was injected over 306 days. During surfactant imbibition, no oil droplets or blobs with sizes large enough to detect with the naked eye appeared on the surfaces of the core. All of the produced oil was in the form of emulsion.

The oil recovery and oil saturation versus time are shown in Figure 4.36. The final oil recovery after 306 days was 87% OOIP and the final oil saturation was 0.13. Although oil was still being produced, the experiment was stopped to measure the

permeability of the core. The brine permeability of the core was 18 md. The final oil recovery determined from weighing the core after 306 days of surfactant imbibition was 85% OOIP, which is in good agreement with the value based on the emulsion density.

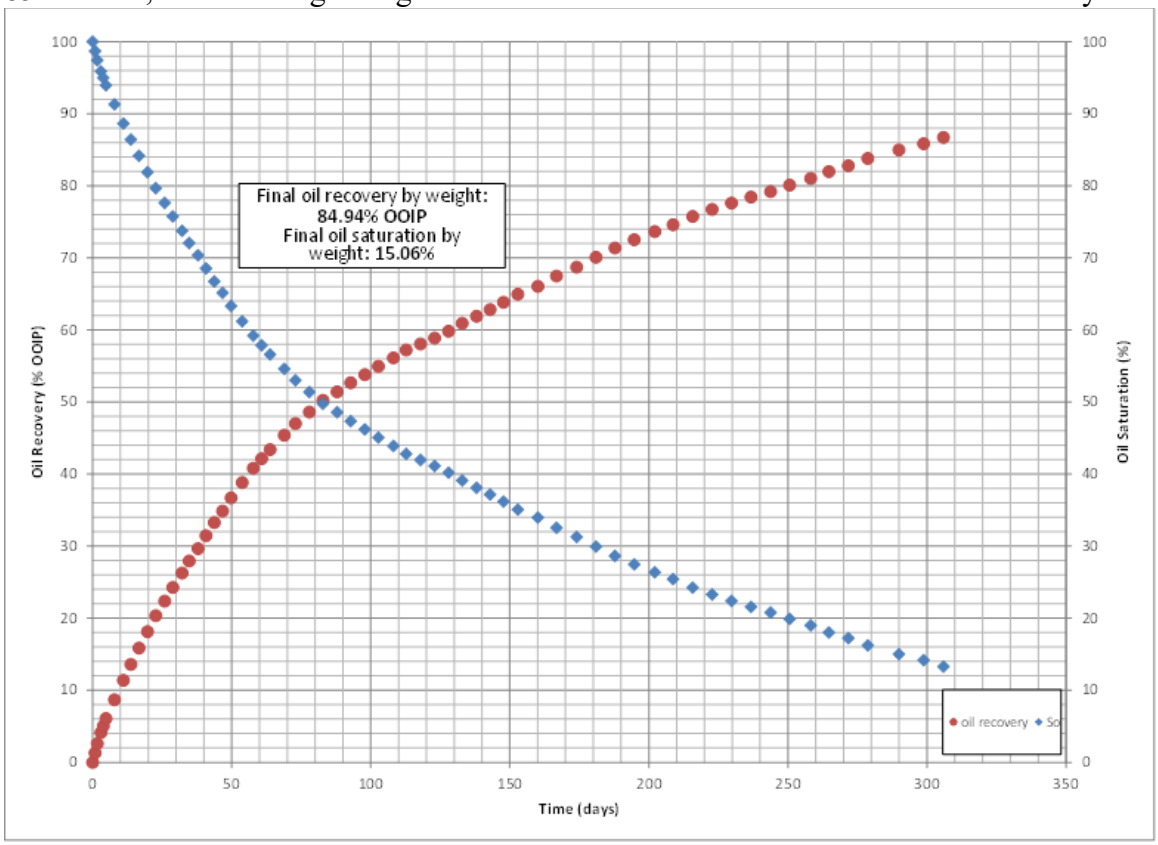


Figure 4.36: Experiment IE 34 oil recovery and oil saturation versus time.

Experiment IE 23

A 3.78 cm diameter by 9.42 cm height (length) Texas cream limestone outcrop core was used for experiment IE 23. To prepare for imbibition, the core was initially fully vacuum-saturated with McElroy dead oil at 23 ºC. The core was then aged in McElroy oil at 75 ºC for 9 days. After preparation, the core was first immersed in 47,500 ppm NaCl brine inside the imbibition cell at 23 ºC to observe oil recovery. No oil was recovered

after 64 hours, which indicated that aging the core at 75 ºC for 9 days had rendered it oil-wet. Figure 4.37 shows a photograph of the core after 64 hours of brine imbibition.

Figure 4.37: Experiment IE 23 did not produce any oil after 64 hours of brine imbibition.

After brine imbibition, the core was immersed in an aqueous solution of 0.85 wt% C12-13-13PO-Sulfate, 0.15 wt% C15-18-IOS, and 2.0 wt% Phenol-1PO-2EO and at 23 ºC. The salinity of the surfactant solution was 47,500 ppm NaCl, which was the optimal salinity with NaCl. After about 24 days of surfactant imbibition, a denser phase precipitated out of the aqueous solution and settled on the bottom of the imbibition cell as shown in Figure 4.38. The aqueous solution seemed to be unstable at a salinity of 47,500 ppm NaCl and a temperature of 23 °C. Subsequent aqueous solution was injected at a salinity of 46,000 and then 45,000 ppm NaCl. Phase precipitation was not observed after decreasing the salinity to 45,000 ppm NaCl. The oil was produced in the form of an emulsion, causing the color of the liquid surrounding the core to gradually change from clear to dark as shown in Figure 4.39. About 50 ml of fresh surfactant solution was flowed into the cell to flush out about 50 ml of the emulsion once each 1 to 4 days to

measure the oil content in the emulsion. About 106 PVs of fresh surfactant solution was injected over 138 days. During surfactant imbibition, no oil droplets or blobs with sizes large enough to detect with the naked eye appeared on the surfaces of the core. All of the produced oil was in the form of emulsion.

Figure 4.38: Aqueous solution unstable at 47,500 ppm NaCl and at 23 °C.

Figure 4.39: Oil was produced as emulsion.

The oil recovery and oil saturation versus time are shown in Figure 4.40. The final oil recovery after 138 days was 47% OOIP and the final oil saturation was 0.53. Although oil was still being produced, the experiment was stopped to measure the permeability of the core. The brine permeability of the core was 8 md. The final oil recovery determined from weighing the core after 138 days of surfactant imbibition was 39% OOIP, which is in good agreement with the value based on the emulsion density.

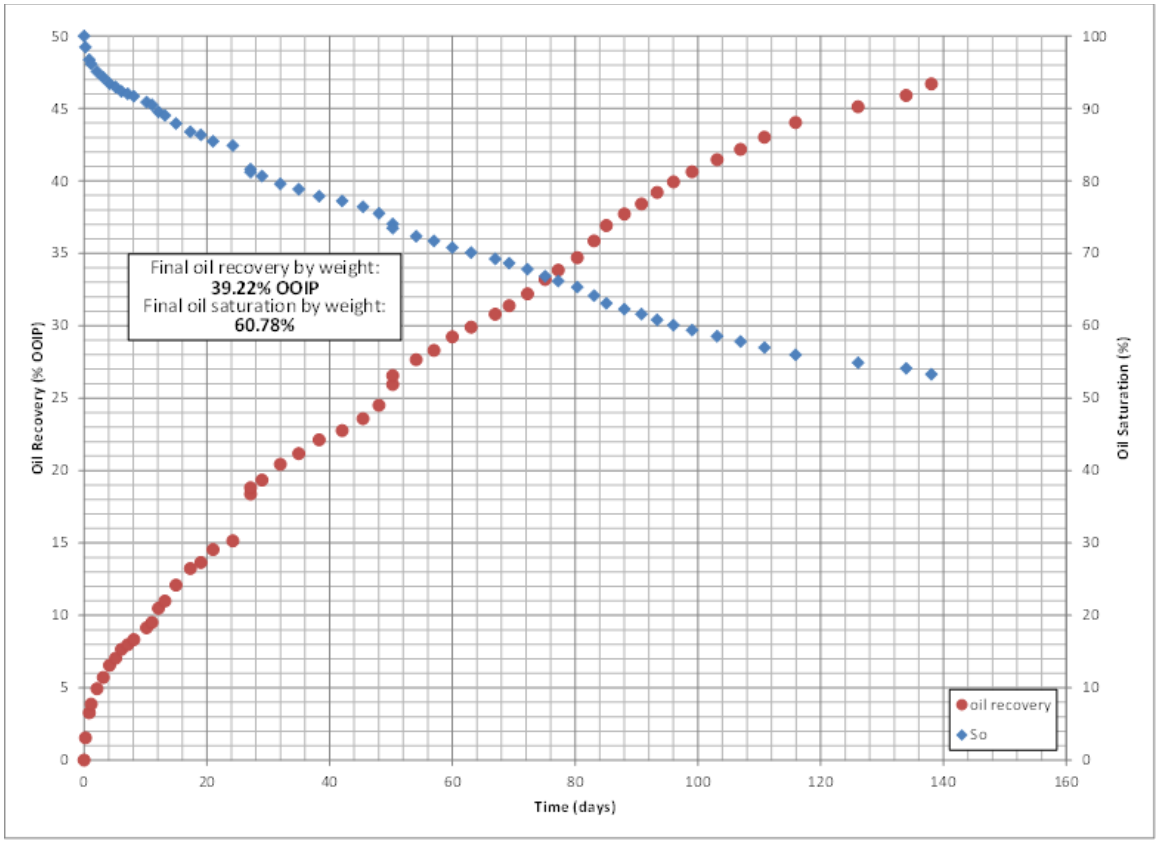


Figure 4.40: Experiment IE 23 oil recovery and oil saturation versus time.

Experiment IE 24

A 3.77 cm diameter by 9.57 cm height (length) Texas cream limestone outcrop core was used for experiment IE 24. To prepare for imbibition, the core was initially fully vacuum-saturated with McElroy dead oil at 23 ºC. The core was then aged in McElroy oil at 75 ºC for 9 days. After preparation, the core was first immersed in 30,000 ppm NaCl brine inside the imbibition cell at 23 °C to observe oil recovery. After 64 hours of brine imbibition, several small oil droplets appeared on the top surface of the core as shown in Figure 4.41. The oil droplets were always attached to the top surface of the core and did not rise up to the air-brine interface.

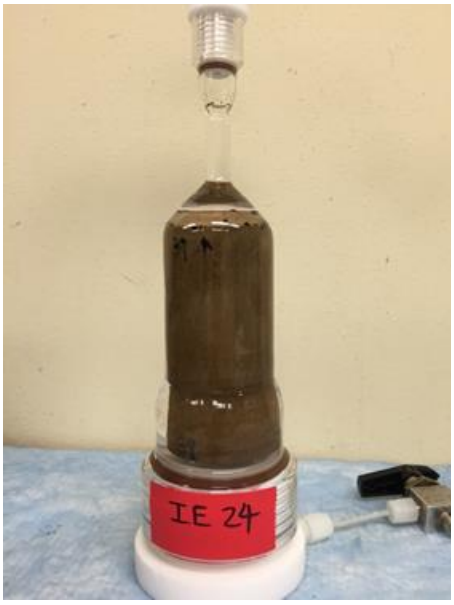


Figure 4.41: Several small oil droplets on the top surface of the core after 64 hours of brine imbibition.

After brine imbibition, the core was immersed in an aqueous solution of 0.85 wt% C12-13-13PO-Sulfate, 0.15 wt% C15-18-IOS, and 0 wt% Phenol-1PO-2EO and at 23 ºC. The salinity of the surfactant solution was 30,000 ppm NaCl, which was the optimal salinity with NaCl. The oil was produced in the form of an emulsion, causing the color of the liquid surrounding the core to gradually change from clear to dark as shown in Figure 4.42. About 50 ml of fresh surfactant solution was flowed into the cell to flush out about 50 ml of the emulsion once each 1 to 4 days to measure the oil content in the emulsion. About 96 PVs of fresh surfactant solution was injected over 138 days. During surfactant imbibition, no oil droplets or blobs with sizes large enough to detect with the naked eye appeared on the surfaces of the core. All of the produced oil was in the form of emulsion.

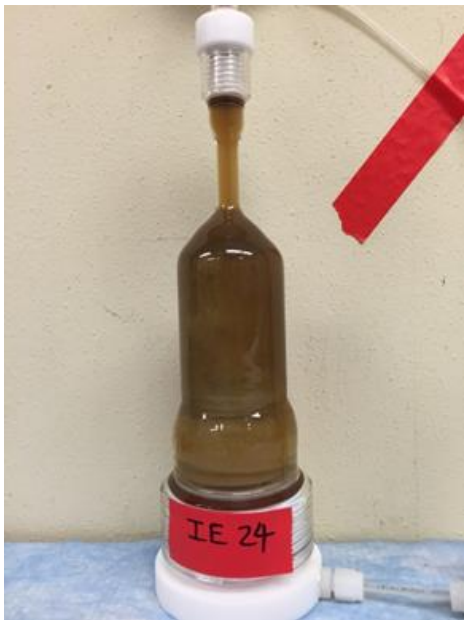


Figure 4.42: Oil was produced as emulsion.

The oil recovery and oil saturation versus time are shown in Figure 4.43. The final oil recovery after 138 days was 56% OOIP and the final oil saturation was 0.44. Although oil was still being produced, the experiment was stopped to measure the permeability of the core. The brine permeability of the core was 5 md. The final oil recovery determined from weighing the core after 138 days of surfactant imbibition was 30% OOIP, which differs significantly from the value based on the emulsion density.

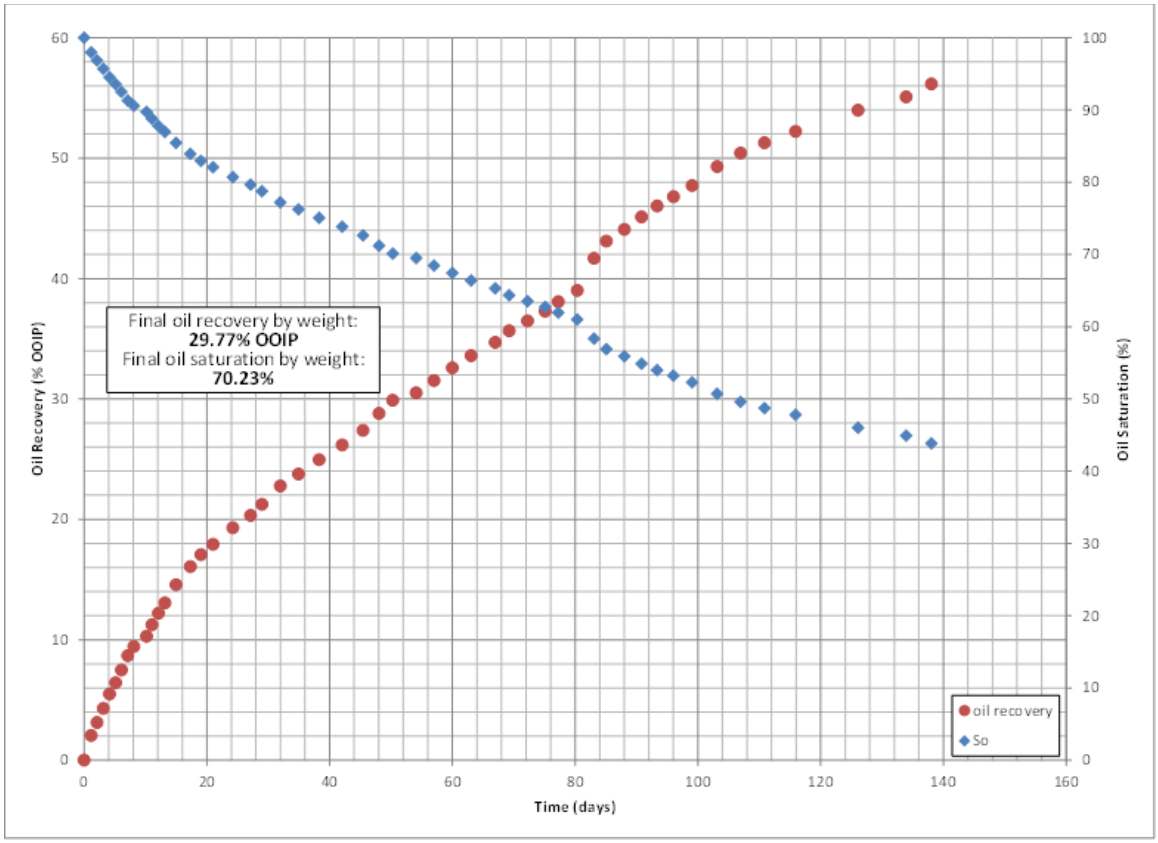


Figure 4.43: Experiment IE 24 oil recovery and oil saturation versus time.

Experiment IE 33

A 3.78 cm diameter by 10.03 cm height (length) Texas cream limestone outcrop core was used for experiment IE 33. To prepare for imbibition, the core was initially fully vacuum-saturated with McElroy dead oil at 23 ºC. The core was then aged in McElroy oil at 23 ºC for 17 days. After preparation, the core was first immersed in 27,500 ppm NaCl brine inside the imbibition cell at 23 °C to observe oil recovery. No oil was recovered after 24 hours, which indicated that aging the core at 23 ºC for 17 days had rendered it oil-wet. Figure 4.44 shows a photograph of the core after 24 hours of brine imbibition.

Figure 4.44: Experiment IE 33 did not produce any oil after 24 hours of brine imbibition.

After brine imbibition, the core was immersed in an aqueous solution of 0.85 wt% C12-13-13PO-Sulfate, 0.15 wt% C15-18-IOS, and 1.0 wt% Phenol-1PO-2EO and at 23 ºC. The salinity of the surfactant solution was 27,500 ppm NaCl, which was a Winsor Type I salinity with NaCl. The oil was produced in the form of an emulsion, causing the color of the liquid surrounding the core to gradually change from clear to dark as shown in Figure 4.45. At the beginning of the experiment, about 50 ml of fresh surfactant solution was flowed into the cell to flush out about 50 ml of the emulsion once per day to measure the oil content in the emulsion. After about 47 days of surfactant imbibition, about 50 ml of the emulsion was flushed out once each 3 to 7 days to measure the oil content. About 160 PVs of fresh surfactant solution was injected over 306 days. During surfactant imbibition, no oil droplets or blobs with sizes large enough to detect with the naked eye appeared on the surfaces of the core. All of the produced oil was in the form of emulsion.

Figure 4.45: Oil was produced as emulsion.

The oil recovery and oil saturation versus time are shown in Figure 4.46. The final oil recovery after 306 days was 66% OOIP and the final oil saturation was 0.34. Although oil was still being produced, the experiment was stopped to measure the permeability of the core. The brine permeability of the core was 11 md. The final oil recovery determined from weighing the core after 306 days of surfactant imbibition was 77% OOIP, which is in good agreement with the value based on the emulsion density.

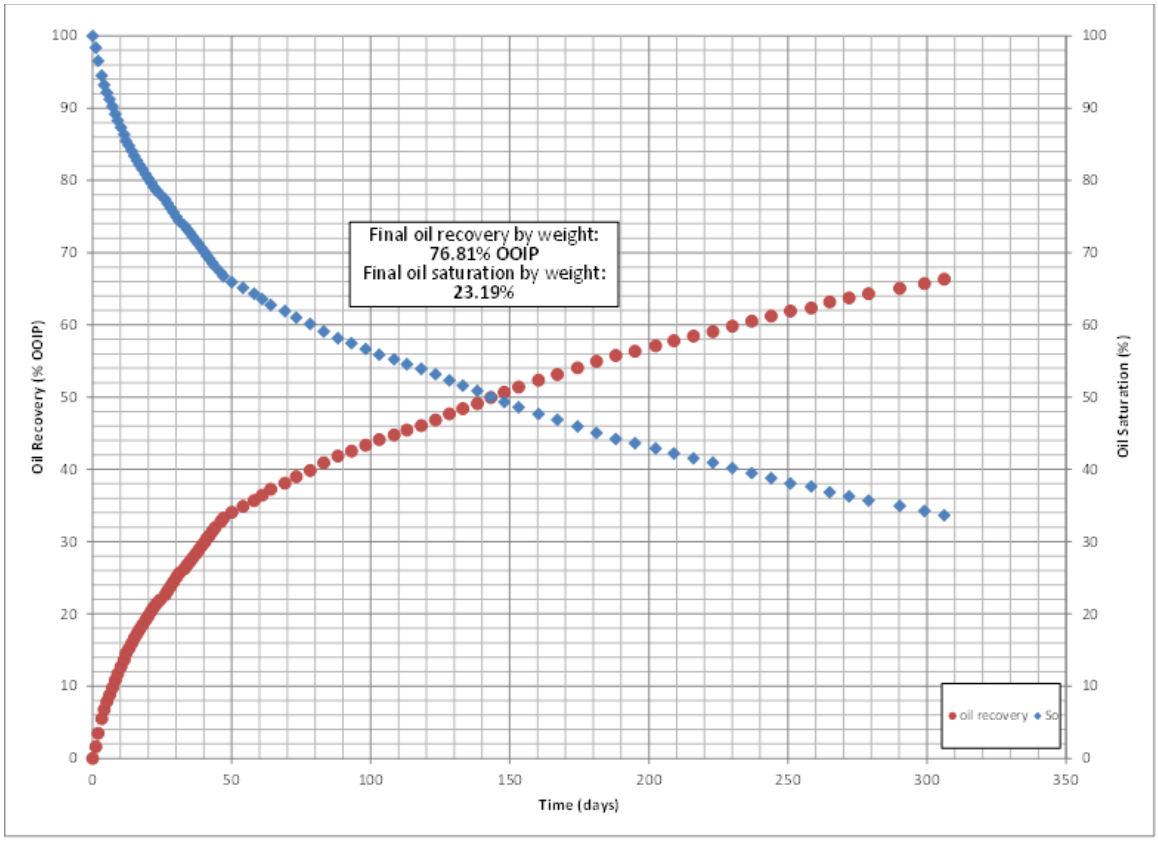


Figure 4.46: Experiment IE 33 oil recovery and oil saturation versus time.

Experiment IE 46

A 3.75 cm diameter by 9.90 cm height (length) Texas cream limestone outcrop core was used for experiment IE 46. To prepare for imbibition, the core was initially fully vacuum-saturated with McElroy dead oil at 23 ºC. The core was then aged in McElroy oil at 23 ºC for 9 days. After preparation, the core was first immersed in 10,000 ppm NaCl brine inside the imbibition cell at 23 °C to observe oil recovery. No oil was recovered after 21 hours, which indicated that aging the core at 23 ºC for 9 days had rendered it oil-wet.

After brine imbibition, the core was immersed in an aqueous solution of 0.85 wt% C12-13-13PO-Sulfate, 0.15 wt% C15-18-IOS, and 1.0 wt% Phenol-1PO-2EO and at 23

ºC. The salinity of the surfactant solution was 10,000 ppm NaCl, which was a Winsor Type I salinity with NaCl. The oil was produced in the form of an emulsion, causing the color of the liquid surrounding the core to gradually change from clear to dark. At the beginning of the experiment, about 50 ml of fresh surfactant solution was flowed into the cell to flush out about 50 ml of the emulsion once per 2 days to measure the oil content in the emulsion. After about 122 days of surfactant imbibition, about 50 ml of the emulsion was flushed out once each 4 to 8 days to measure the oil content. About 155 PVs of fresh surfactant solution was injected over 217 days. During surfactant imbibition, no oil droplets or blobs with sizes large enough to detect with the naked eye appeared on the surfaces of the core. All of the produced oil was in the form of emulsion.

The oil recovery and oil saturation versus time are shown in Figure 4.47. The final oil recovery after 217 days was 42% OOIP and the final oil saturation was 0.58. Although oil was still being produced, the experiment was stopped to measure the permeability of the core. The brine permeability of the core was 9 md. The final oil recovery determined from weighing the core after 217 days of surfactant imbibition was 49% OOIP, which is in good agreement with the value based on the emulsion density.

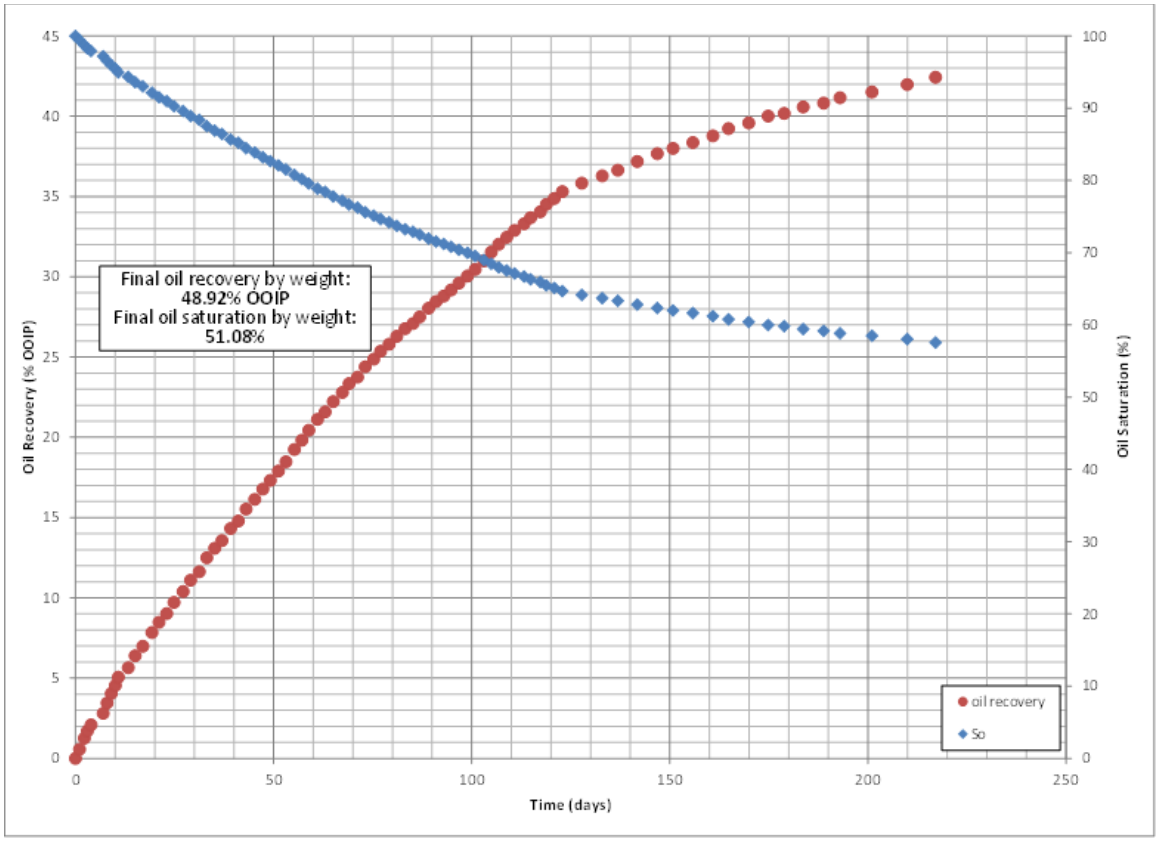


Figure 4.47: Experiment IE 46 oil recovery and oil saturation versus time.

Experiment IE 35

A 3.77 cm diameter by 9.57 cm height (length) Texas cream limestone outcrop core was used for experiment IE 35. To prepare for imbibition, the core was initially fully vacuum-saturated with McElroy dead oil at 23 ºC. The core was then aged in McElroy oil at 23 ºC for 30 days. After preparation, the core was first immersed in 33,000 ppm NaCl brine inside the imbibition cell at 23 °C to observe oil recovery. No oil was recovered after 32 hours, which indicated that aging the core at 23 ºC for 30 days had rendered it oil-wet.

After brine imbibition, the core was immersed in an aqueous solution of 0.2125 wt% C12-13-13PO-Sulfate, 0.0375 wt% C15-18-IOS, and 0.25 wt% Phenol-1PO-2EO

and at 23 ºC. The salinity of the surfactant solution was 33,000 ppm NaCl, which was the optimal salinity with NaCl. The oil was produced in the form of an emulsion, causing the color of the liquid surrounding the core to gradually change from clear to dark. About 50 ml of fresh surfactant solution was flowed into the cell to flush out about 50 ml of the emulsion once per week to measure the oil content in the emulsion. About 56 PVs of fresh surfactant solution was injected over 254 days. During surfactant imbibition, no oil droplets or blobs with sizes large enough to detect with the naked eye appeared on the surfaces of the core. All of the produced oil was in the form of emulsion.

The oil recovery and oil saturation versus time are shown in Figure 4.48. The final oil recovery after 254 days was 43% OOIP and the final oil saturation was 0.57. Although oil was still being produced, the experiment was stopped to measure the permeability of the core. The brine permeability of the core was 44 md. The final oil recovery determined from weighing the core after 254 days of surfactant imbibition was 49% OOIP, which is in good agreement with the value based on the emulsion density.

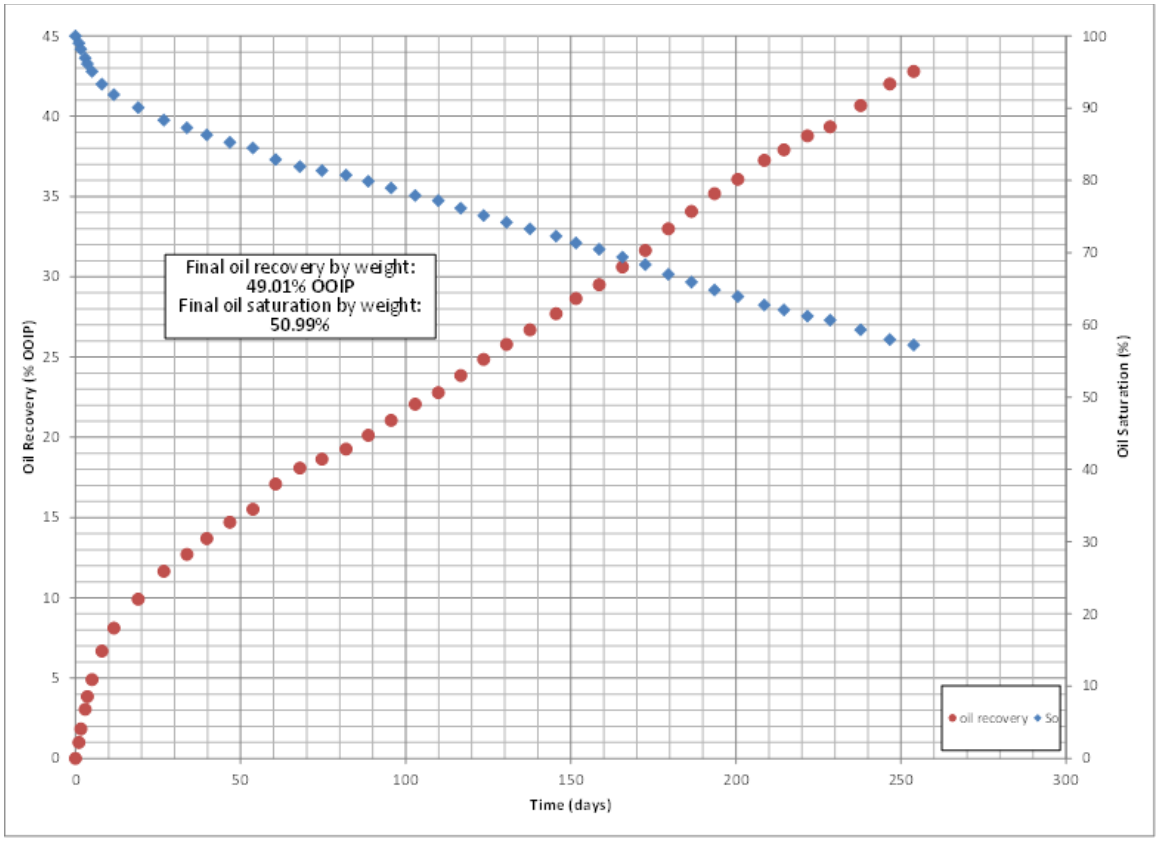


Figure 4.48: Experiment IE 35 oil recovery and oil saturation versus time.

Experiment IE 48

A 3.76 cm diameter by 9.86 cm height (length) Texas cream limestone outcrop core was used for experiment IE 48. To prepare for imbibition, the core was initially fully vacuum-saturated with McElroy dead oil at 23 ºC. The core was then aged in McElroy oil at 23 ºC for 8 days. After preparation, the core was first immersed in 37,500 ppm NaCl brine inside the imbibition cell at 23 °C to observe oil recovery. No oil was recovered after 20 hours, which indicated that aging the core at 23 ºC for 8 days had rendered it oil-wet.

After brine imbibition, the core was immersed in an aqueous solution of 0.425 wt% C12-13-13PO-Sulfate, 0.075 wt% C15-18-IOS, and 0.5 wt% Phenol-1PO-2EO and

at 23 ºC. The salinity of the surfactant solution was 37,500 ppm NaCl, which was the optimal salinity with NaCl. The oil was produced in the form of an emulsion, causing the color of the liquid surrounding the core to gradually change from clear to dark. About 50 ml of fresh surfactant solution was flowed into the cell to flush out about 50 ml of the emulsion once each 2 to 7 days to measure the oil content in the emulsion. The emulsion was flushed out more frequently at the beginning of the experiment than at later times. About 73 PVs of fresh surfactant solution was injected over 136 days. During surfactant imbibition, no oil droplets or blobs with sizes large enough to detect with the naked eye appeared on the surfaces of the core. All of the produced oil was in the form of emulsion.

The oil recovery and oil saturation versus time are shown in Figure 4.49. The final oil recovery after 136 days was 31% OOIP and the final oil saturation was 0.69. Although oil was still being produced, the experiment was stopped to measure the permeability of the core. The brine permeability of the core was 9 md. The final oil recovery determined from weighing the core after 136 days of surfactant imbibition was 40% OOIP, which differs from the value based on the emulsion density.

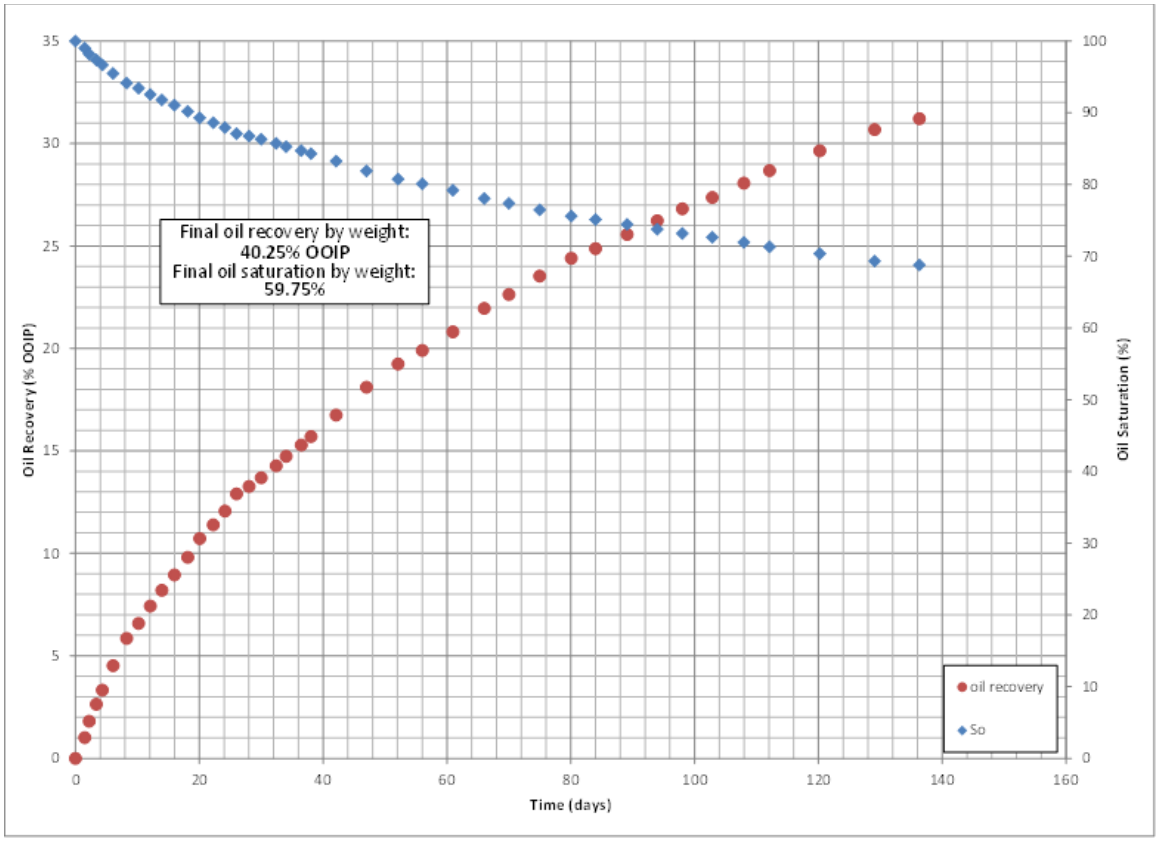


Figure 4.49: Experiment IE 48 oil recovery and oil saturation versus time.

Experiment IE 17

A 3.80 cm diameter by 10.06 cm height (length) Silurian dolomite outcrop core was used for experiment IE 17. To prepare for imbibition, the core was initially fully vacuum-saturated with McElroy dead oil at 23 ºC. The core was not aged in oil. After preparation, the core was first immersed in 27,500 ppm NaCl brine inside the imbibition cell at 23 °C to observe oil recovery. No oil was recovered after 12 hours, which indicated that the core was oil-wet. Figure 4.50 shows a photograph of the core after 12 hours of brine imbibition.

Figure 4.50: Experiment IE 17 did not produce any oil after 12 hours of brine imbibition.

After brine imbibition, the core was immersed in an aqueous solution of 0.85 wt% C12-13-13PO-Sulfate, 0.15 wt% C15-18-IOS, and 1.0 wt% IBA and at 23 ºC. The salinity of the surfactant solution was 27,500 ppm NaCl, which was the optimal salinity with NaCl. The oil was produced in the form of an emulsion, causing the color of the liquid surrounding the core to gradually change from clear to dark as shown in Figure 4.51. About 100 ml of fresh surfactant solution was flowed into the cell to flush out about 100 ml of the emulsion once each 1 to 4 days to measure the oil content in the emulsion. About 52 PVs of fresh surfactant solution was injected over 12 days. During surfactant imbibition, no oil droplets or blobs with sizes large enough to detect with the naked eye appeared on the surfaces of the core. All of the produced oil was in the form of emulsion.

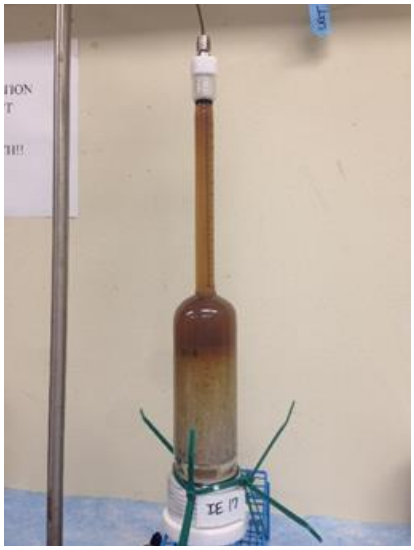


Figure 4.51: Oil was produced as emulsion.

The oil recovery and oil saturation versus time are shown in Figure 4.52. The final oil recovery after 12 days was 45% OOIP and the final oil saturation was 0.55. The permeability of the core was not measured. The final oil recovery determined from weighing the core after 12 days of surfactant imbibition was 45% OOIP, which is in good agreement with the value based on the emulsion density.

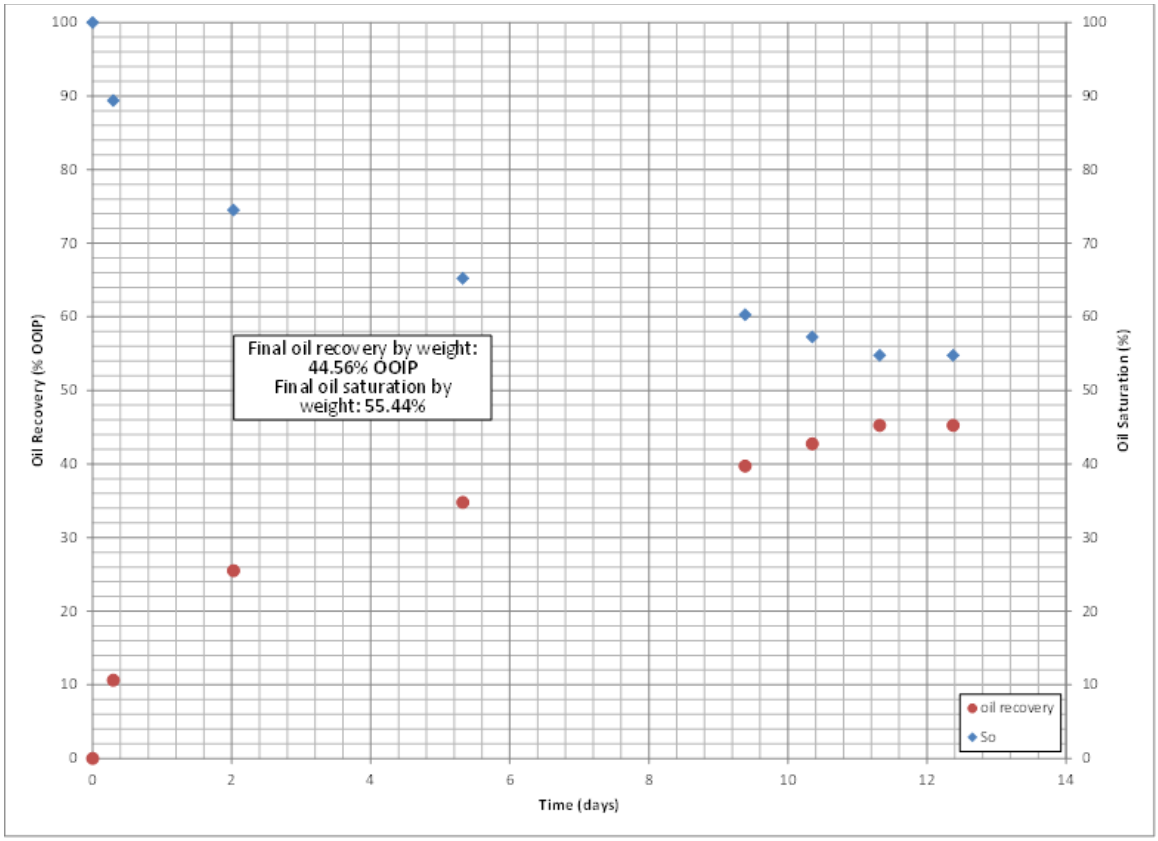


Figure 4.52: Experiment IE 17 oil recovery and oil saturation versus time.

Experiment IE 18

A 3.79 cm diameter by 9.85 cm height (length) Silurian dolomite outcrop core was used for experiment IE 18. To prepare for imbibition, the core was initially fully vacuum-saturated with McElroy dead oil at 23 ºC. The core was not aged in oil. After preparation, the core was first immersed in 27,500 ppm NaCl brine inside the imbibition cell at 23 °C to observe oil recovery. No oil was recovered after 15 hours, which indicated that the core was oil-wet. Figure 4.53 shows a photograph of the core after 15 hours of brine imbibition.

Figure 4.53: Experiment IE 18 did not produce any oil after 15 hours of brine imbibition.

After brine imbibition, the core was immersed in an aqueous solution of 0.85 wt% C12-13-13PO-Sulfate, 0.15 wt% C15-18-IOS, and 1.0 wt% IBA and at 23 ºC. The salinity of the surfactant solution was 27,500 ppm NaCl, which was the optimal salinity with NaCl. The oil was produced in the form of an emulsion, causing the color of the liquid surrounding the core to gradually change from clear to dark as shown in Figure 4.54. Experiment IE 18 was a completely static imbibition experiment. Fresh surfactant solution was not flowed into the cell to flush out the emulsion. During surfactant imbibition, no oil droplets or blobs with sizes large enough to detect with the naked eye appeared on the surfaces of the core. All of the produced oil was in the form of emulsion.

Figure 4.54: Oil was produced as emulsion.

The oil recovery was not able to be measured during the duration of the experiment because the emulsion was not flushed out regularly to measure its oil content. The final oil recovery (measured at the end of surfactant imbibition) after 10 days was 38% OOIP and the final oil saturation was 0.62. The permeability of the core was not measured. The final oil recovery determined from weighing the core after 10 days of surfactant imbibition was 35% OOIP, which is in good agreement with the value based on the emulsion density.

Experiment IE 19

A 3.80 cm diameter by 10.00 cm height (length) Silurian dolomite outcrop core was used for experiment IE 19. To prepare for imbibition, the core was initially fully vacuum-saturated with McElroy dead oil at 23 ºC. The core was not aged in oil. After preparation, the core was first immersed in 40,000 ppm NaCl brine inside the imbibition cell at 23 °C to observe oil recovery. No oil was recovered after 21 hours, which

indicated that the core was oil-wet. Figure 4.55 shows a photograph of the core after 21 hours of brine imbibition.

Figure 4.55: Experiment IE 19 did not produce any oil after 21 hours of brine imbibition.

After brine imbibition, the core was immersed in an aqueous solution of 0.85 wt% C12-13-13PO-Sulfate, 0.15 wt% C15-18-IOS, and 1.0 wt% Phenol-1PO-2EO and at 23 ºC. The salinity of the surfactant solution was 40,000 ppm NaCl, which was the optimal salinity with NaCl. The oil was produced in the form of an emulsion, causing the color of the liquid surrounding the core to gradually change from clear to dark as shown in Figure 4.56. At the beginning of the experiment, about 25 to 50 ml of fresh surfactant solution was flowed into the cell to flush out about 25 to 50 ml of the emulsion once per day to measure the oil content in the emulsion. After about 47 days of surfactant imbibition, the emulsion was flushed out once each 3 to 17 days to measure the oil content. About 107 PVs of fresh surfactant solution was injected over 130 days. During surfactant imbibition, no oil droplets or blobs with sizes large enough to detect with the naked eye appeared on the surfaces of the core. All of the produced oil was in the form of emulsion.

Figure 4.56: Oil was produced as emulsion.

The oil recovery and oil saturation versus time are shown in Figure 4.57. The final oil recovery after 130 days was 93% OOIP and the final oil saturation was 0.07. After the oil production had plateaued, the experiment was stopped to measure the permeability of the core. The brine permeability of the core was 58 md. The final oil recovery determined from weighing the core after 130 days of surfactant imbibition was 97% OOIP, which is in good agreement with the value based on the emulsion density.

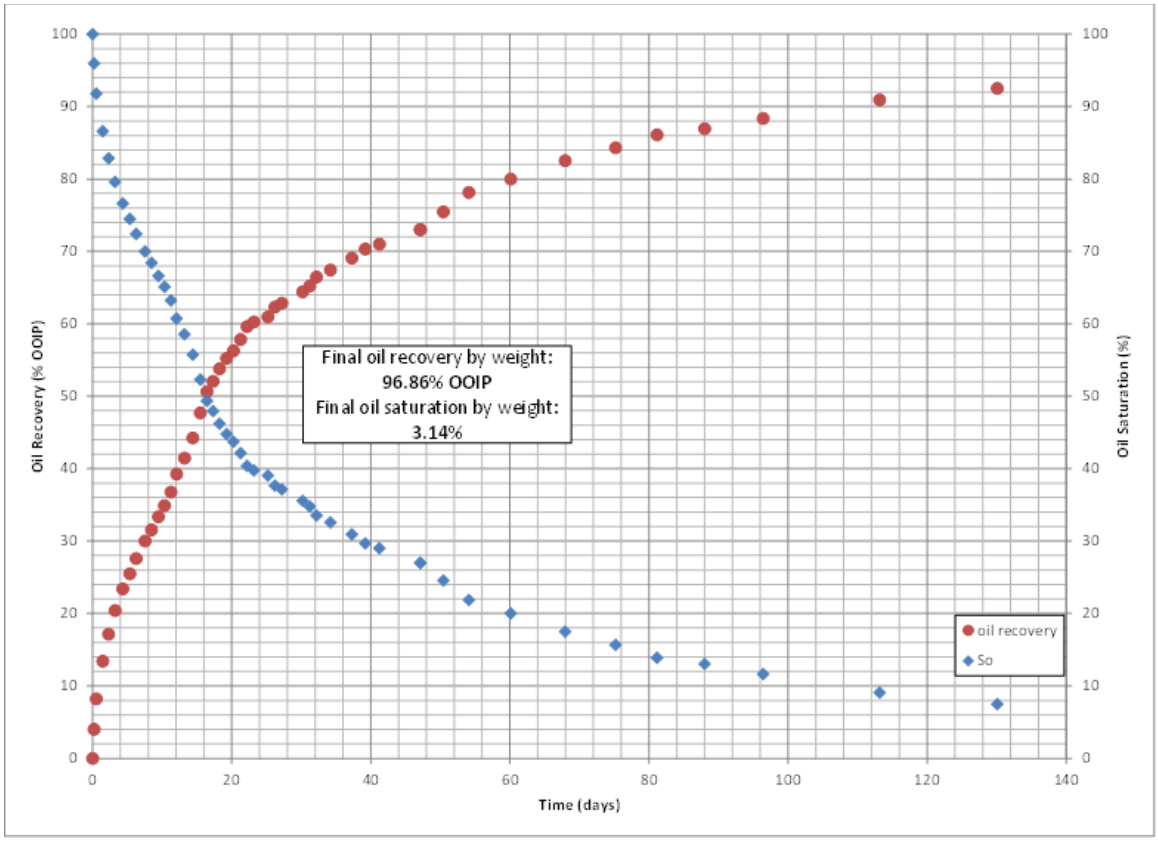


Figure 4.57: Experiment IE 19 oil recovery and oil saturation versus time.

Experiment IE 30

A 3.80 cm diameter by 10.25 cm height (length) Silurian dolomite outcrop core was used for experiment IE 30. To prepare for imbibition, the core was initially fully vacuum-saturated with Oregon Basin surrogate oil (diluted with 20 wt% decalin) at 45 ºC. The core was not aged in oil. After preparation, the core was first immersed in 43,000 ppm NaCl brine inside the imbibition cell at 45 °C to observe oil recovery. About 2.9 ml of oil was recovered after 22 hours of brine imbibition.

After brine imbibition, the core was immersed in an aqueous solution of 0.5 wt% TDA-13PO-Sulfate, 0.5 wt% C20-24-IOS, and 0.5 wt% Phenol-1PO-5EO and at 45 ºC. The salinity of the surfactant solution was 43,167 ppm TDS consisting of 37,500 ppm

Na2CO3, which was the optimal salinity with SSOBB synthetic brine. The oil was produced in the form of an emulsion, causing the color of the liquid surrounding the core to gradually change from clear to dark as shown in Figure 4.58. About 50 ml of fresh surfactant solution was flowed into the cell to flush out about 50 ml of the emulsion once per day to measure the oil content in the emulsion. About 110 PVs of fresh surfactant solution was injected over 44 days. During surfactant imbibition, no oil droplets or blobs with sizes large enough to detect with the naked eye appeared on the surfaces of the core. All of the produced oil was in the form of emulsion.

Figure 4.58: Oil was produced as emulsion.

The oil recovery and oil saturation versus time are shown in Figure 4.59. The final oil recovery after 44 days was 133% OOIP and the final oil saturation was -0.27. The experiment was stopped to measure the permeability of the core. The brine permeability of the core was 63 md. The final oil recovery determined from weighing the core after 44 days of surfactant imbibition was 78% OOIP, which differs significantly from the value based on the emulsion density.

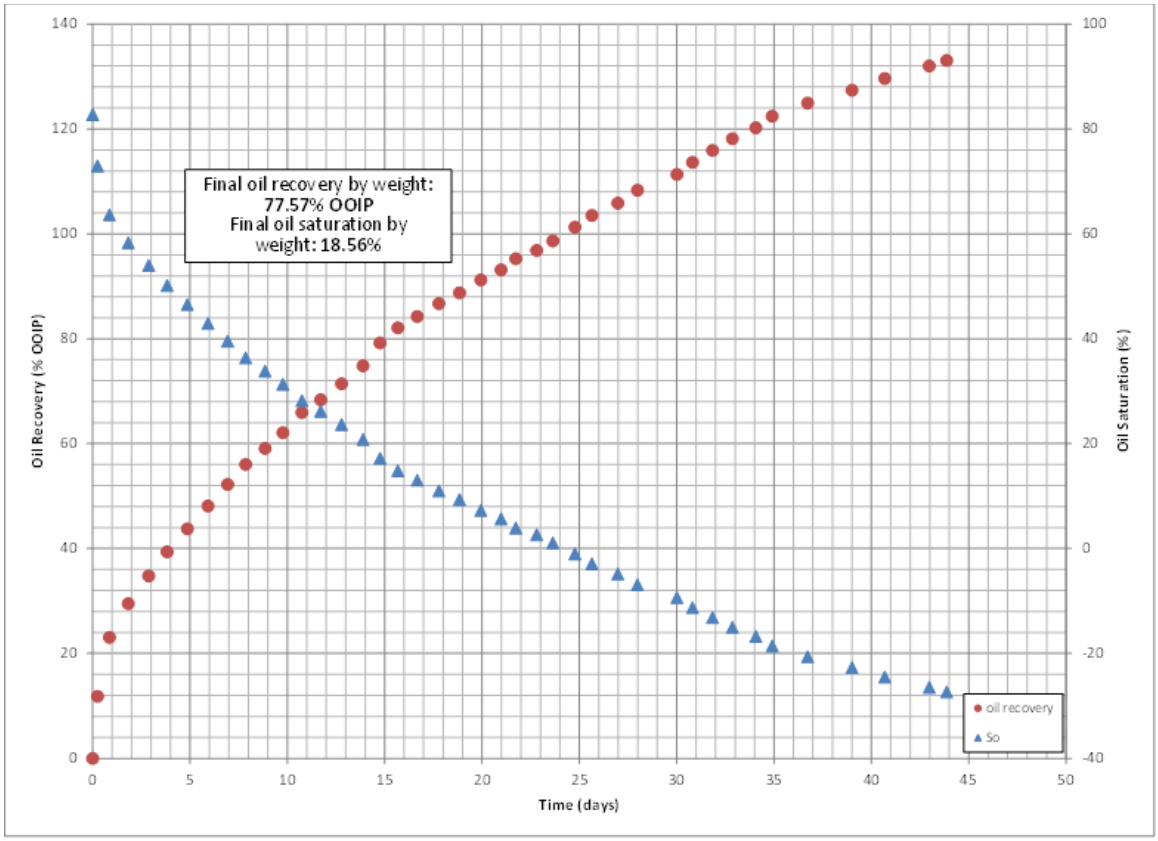


Figure 4.59: Experiment IE 30 oil recovery and oil saturation versus time.

Experiment IE 32

A 3.77 cm diameter by 9.43 cm height (length) Texas cream limestone outcrop core was used for experiment IE 32. To prepare for imbibition, the core was initially fully vacuum-saturated with RBD dead oil at 23 ºC. The core was then aged in RBD oil at 23 ºC for 13 days. After preparation, the core was first immersed in 58,500 ppm NaCl brine inside the imbibition cell at 23 °C to observe oil recovery. No oil was recovered after 41 hours, which indicated that aging the core at 23 ºC for 13 days had rendered it oil-wet. Figure 4.60 shows a photograph of the core after 41 hours of brine imbibition.

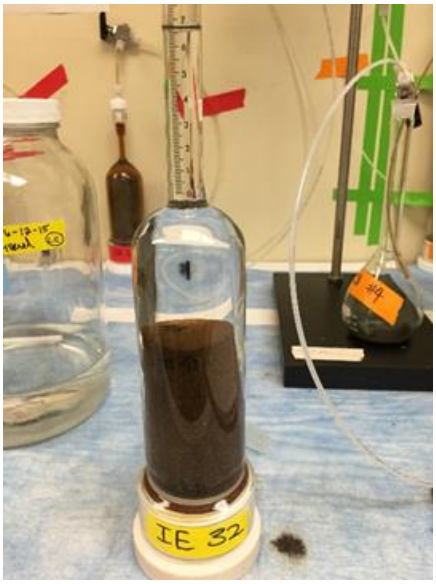


Figure 4.60: Experiment IE 32 did not produce any oil after 41 hours of brine imbibition.

After brine imbibition, the core was immersed in an aqueous solution of 0.1 wt% TDA-13PO-Sulfate, 0.2 wt% C20-24-IOS, 0.2 wt% TDA-45PO-10EO-Sulfate, and 0.25 wt% 2-Ethylhexanol-7PO-Sulfate and at 23 ºC. The salinity of the surfactant solution was 58,500 ppm Na2CO3, which was the optimal salinity with Na2CO3. The oil was produced in the form of an emulsion, causing the color of the liquid surrounding the core to gradually change from clear to dark as shown in Figure 4.61. About 50 ml of fresh surfactant solution was flowed into the cell to flush out about 50 ml of the emulsion once per day to measure the oil content in the emulsion. About 66 PVs of fresh surfactant solution was injected over 34 days. During surfactant imbibition, no oil droplets or blobs with sizes large enough to detect with the naked eye appeared on the surfaces of the core. All of the produced oil was in the form of emulsion.

Figure 4.61: Oil was produced as emulsion.

The oil recovery and oil saturation versus time are shown in Figure 4.62. The final oil recovery after 34 days was 63% OOIP and the final oil saturation was 0.37. After 34 days, the experiment was stopped to examine the distribution of oil and water inside the core during surfactant imbibition by cleaving the core vertically as shown in Figure 4.63. The imbibition appeared to occur from the bottom and the sides of the core where the oil appeared to flow mainly in an upward direction along the imbibition front. The flow seemed to be predominantly co-current and governed by gravity forces. The permeability of the core was not measured. The final oil recovery determined from weighing the core after 34 days of surfactant imbibition was 64% OOIP, which is in good agreement with the value based on the emulsion density.

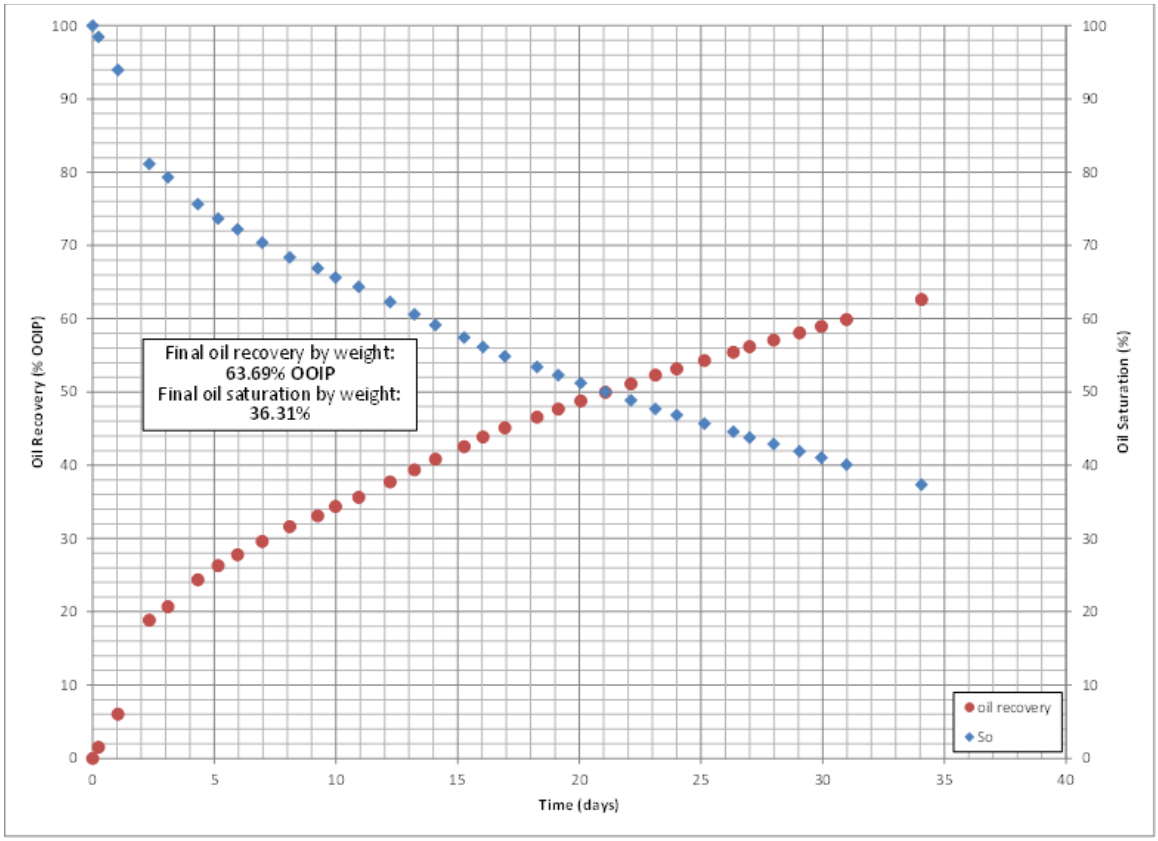


Figure 4.62: Experiment IE 32 oil recovery and oil saturation versus time.

Figure 4.63: Distribution of oil and water inside the core after 34 days of surfactant imbibition.

Experiment IE 44

Experiment IE 44 was a duplicate experiment of IE 32. A 3.75 cm diameter by 9.83 cm height (length) Texas cream limestone outcrop core was used for experiment IE 44. To prepare for imbibition, the core was initially fully vacuum-saturated with RBD dead oil at 23 ºC. The core was then aged in RBD oil at 23 ºC for 12 days. After preparation, the core was first immersed in 58,500 ppm NaCl brine inside the imbibition cell at 23 °C to observe oil recovery. No oil was recovered after 18 hours, which indicated that aging the core at 23 ºC for 12 days had rendered it oil-wet.

After brine imbibition, the core was immersed in an aqueous solution of 0.1 wt% TDA-13PO-Sulfate, 0.2 wt% C20-24-IOS, 0.2 wt% TDA-45PO-10EO-Sulfate, and 0.25 wt% 2-Ethylhexanol-7PO-Sulfate and at 23 ºC. The salinity of the surfactant solution was 58,500 ppm Na2CO3, which was the optimal salinity with Na2CO3. The oil was produced in the form of an emulsion, causing the color of the liquid surrounding the core

to gradually change from clear to dark as shown in Figure 4.64. About 50 ml of fresh surfactant solution was flowed into the cell to flush out about 50 ml of the emulsion once per day to measure the oil content in the emulsion. About 20 PVs of fresh surfactant solution was injected over 11 days. During surfactant imbibition, no oil droplets or blobs with sizes large enough to detect with the naked eye appeared on the surfaces of the core. All of the produced oil was in the form of emulsion.

Figure 4.64: Oil was produced as emulsion.

The oil recovery and oil saturation versus time are shown in Figure 4.65. The final oil recovery after 11 days was 34% OOIP and the final oil saturation was 0.66. After 11 days, the experiment was stopped to examine the distribution of oil and water inside the core during surfactant imbibition by cleaving the core vertically. Figure 4.66 shows a photograph of the inside of the core 5 minutes after it was cleaved. The core appeared to have a uniform fluid distribution with slightly less oil saturation in the center. Figure 4.67 shows a photograph of the inside of the core 2 days after it was cleaved. The fluid distribution changed with time as the oil appeared to have moved to the edges of the core.

The permeability of the core was not measured. The final oil recovery determined from weighing the core after 11 days of surfactant imbibition was 36% OOIP, which is in good agreement with the value based on the emulsion density.

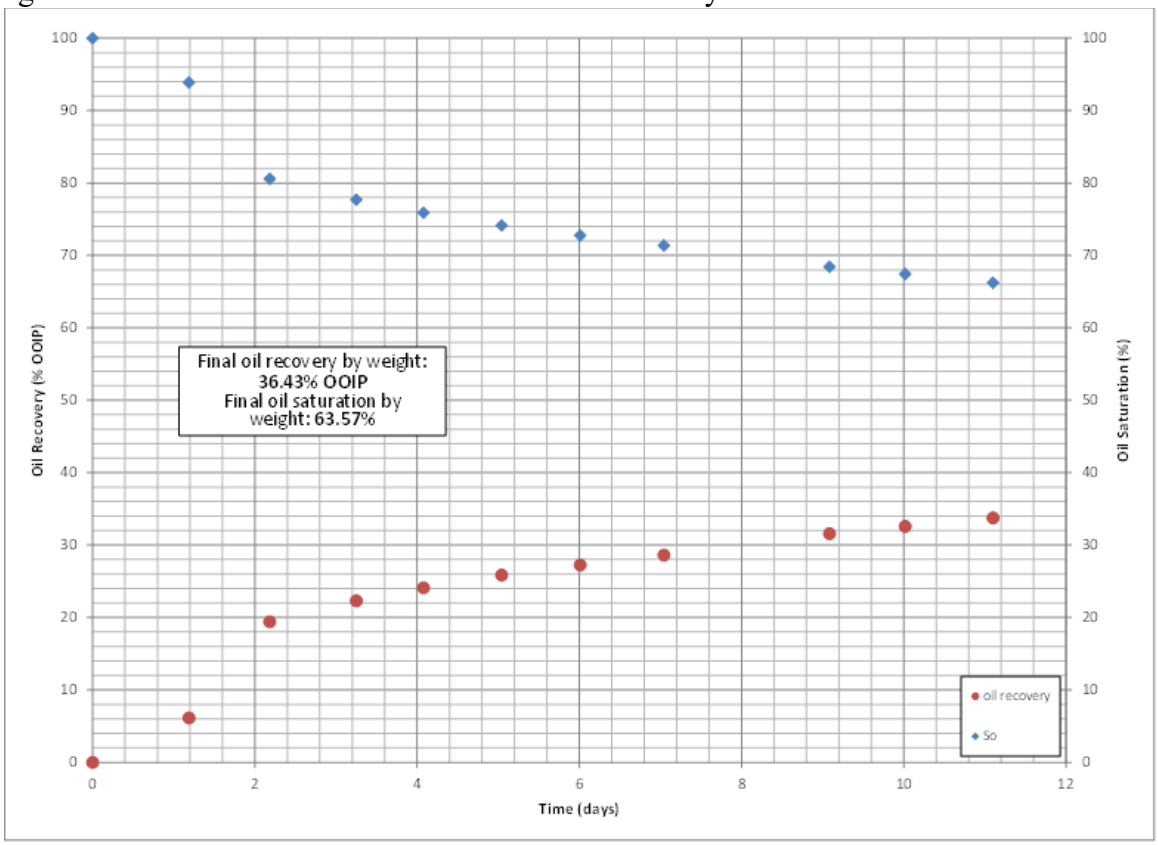


Figure 4.65: Experiment IE 44 oil recovery and oil saturation versus time.

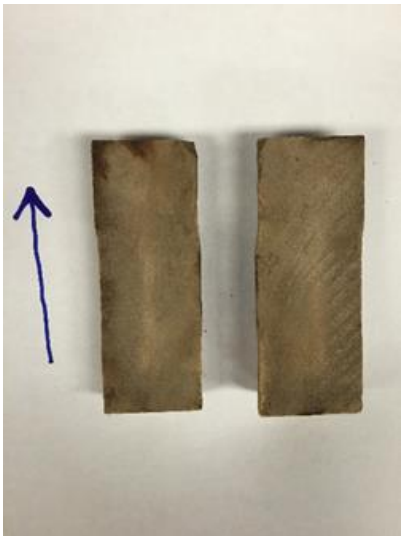


Figure 4.66: Distribution of oil and water inside the core after 11 days of surfactant imbibition. Photograph was taken 5 minutes after the core was cleaved.

Figure 4.67: Distribution of oil and water inside the core after 11 days of surfactant imbibition. Photograph was taken 2 days after the core was cleaved.

Experiment IE 36

A 3.79 cm diameter by 9.91 cm height (length) Silurian dolomite outcrop core was used for experiment IE 36. To prepare for imbibition, the core was initially fully

vacuum-saturated with SAMA surrogate oil (diluted with 10 wt% toluene) at 23 ºC. The core was then aged in SAMA surrogate oil at 23 ºC for 9 days. After preparation, the core was first immersed in 80,000 ppm NaCl brine inside the imbibition cell at 78 °C to observe oil recovery. About 7.4 ml of oil was recovered after 24 hours of brine imbibition.

After brine imbibition, the core was immersed in an aqueous solution of 0.5 wt% C28-25PO-45EO-COO-, 0.2 wt% C15-18-IOS, 0.3 wt% C19-28-IOS, and 1 wt% EDTA and at 78 ºC. The salinity of the surfactant solution was 80,000 ppm TDS, which was the optimal salinity. The oil was produced in the form of an emulsion, causing the color of the liquid surrounding the core to gradually change from clear to dark. About 50 ml of fresh surfactant solution was flowed into the cell to flush out about 50 ml of the emulsion once per day to measure the oil content in the emulsion. About 65 PVs of fresh surfactant solution was injected over 20 days. During surfactant imbibition, no oil droplets or blobs with sizes large enough to detect with the naked eye appeared on the surfaces of the core. All of the produced oil was in the form of emulsion.

The oil recovery and oil saturation versus time are shown in Figure 4.68. The final oil recovery after 20 days was 84% OOIP and the final oil saturation was 0.10. After 20 days, the experiment was stopped to examine the distribution of oil and water inside the core during surfactant imbibition by cleaving the core vertically as shown in Figure 4.69. The imbibition appeared to occur from the bottom and the sides of the core where the oil appeared to flow mainly in an upward direction along the imbibition front. The flow seemed to be predominantly co-current and governed by gravity forces. The permeability of the core was not measured. The final oil recovery determined from weighing the core after 20 days of surfactant imbibition was 15% OOIP, which differs significantly from the value based on the emulsion density.

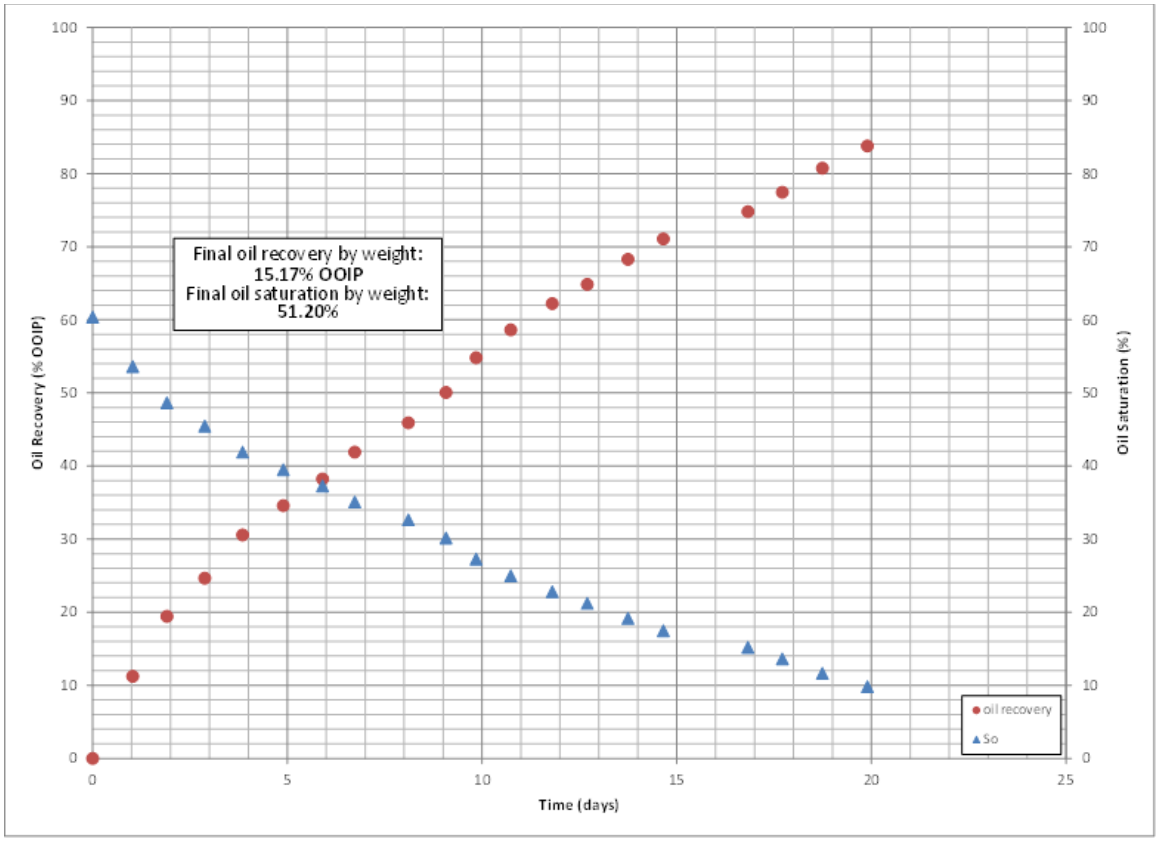


Figure 4.68: Experiment IE 36 oil recovery and oil saturation versus time.

Figure 4.69: Distribution of oil and water inside the core after 20 days of surfactant imbibition.

Experiment IE 37

Experiment IE 37 was a duplicate experiment of IE 36. A 3.78 cm diameter by 9.99 cm height (length) Silurian dolomite outcrop core was used for experiment IE 37. To prepare for imbibition, the core was initially fully vacuum-saturated with SAMA surrogate oil (diluted with 10 wt% toluene) at 23 ºC. The core was then aged in SAMA surrogate oil at 78 ºC for 7 days. After preparation, the core was first immersed in 80,000 ppm NaCl brine inside the imbibition cell at 78 °C to observe oil recovery. About 3.5 ml of oil was recovered after 22 hours of brine imbibition. The core appeared to be more oil-wet after aging at a higher temperature compared to IE 36.

After brine imbibition, the core was immersed in an aqueous solution of 0.5 wt% C28-25PO-45EO-COO-, 0.2 wt% C15-18-IOS, 0.3 wt% C19-28-IOS, and 1 wt% EDTA and at 78 ºC. The salinity of the surfactant solution was 80,000 ppm TDS, which was the optimal salinity. The oil was produced in the form of an emulsion, causing the color of the liquid surrounding the core to gradually change from clear to dark. About 50 ml of fresh surfactant solution was flowed into the cell to flush out about 50 ml of the emulsion once per day to measure the oil content in the emulsion. About 74 PVs of fresh surfactant solution was injected over 27 days. During surfactant imbibition, no oil droplets or blobs with sizes large enough to detect with the naked eye appeared on the surfaces of the core. All of the produced oil was in the form of emulsion.

The oil recovery and oil saturation versus time are shown in Figure 4.70. The final oil recovery after 27 days was 121% OOIP and the final oil saturation was -0.15. The experiment was stopped to measure the permeability of the core. The brine permeability of the core was 30 md. The final oil recovery determined from weighing the core after 27 days of surfactant imbibition was 30% OOIP, which differs significantly from the value based on the emulsion density.

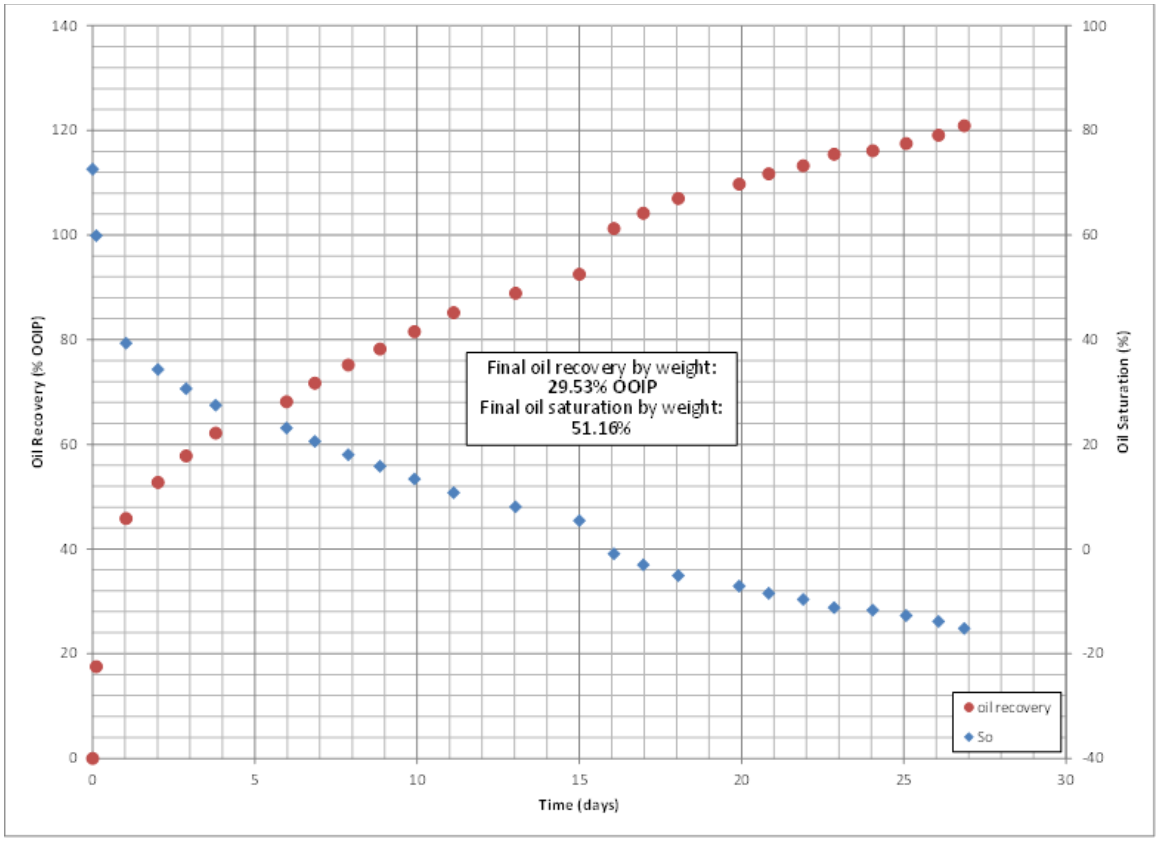


Figure 4.70: Experiment IE 37 oil recovery and oil saturation versus time.

Experiment IE 40

A 3.76 cm diameter by 9.37 cm height (length) Texas cream limestone outcrop core was used for experiment IE 40. To prepare for imbibition, the core was initially fully vacuum-saturated with SAMA surrogate oil (diluted with 10 wt% toluene) at 23 ºC. The core was then aged in SAMA surrogate oil at 78 ºC for 42 days. After preparation, the core was first immersed in 80,000 ppm NaCl brine inside the imbibition cell at 78 °C to observe oil recovery. About 0.6 ml of oil was recovered after 20 hours of brine imbibition. Figure 4.71 shows a photograph of the core after 20 hours of brine imbibition.

Figure 4.71: Experiment IE 40 produced 0.6 ml of oil after 20 hours of brine imbibition.

After brine imbibition, the core was immersed in an aqueous solution of 0.5 wt% C28-25PO-45EO-COO-, 0.2 wt% C15-18-IOS, 0.3 wt% C19-28-IOS, and 1 wt% EDTA and at 78 ºC. The salinity of the surfactant solution was 80,000 ppm TDS, which was the optimal salinity. The oil was produced in the form of an emulsion, causing the color of the liquid surrounding the core to gradually change from clear to dark as shown in Figure 4.72. About 50 ml of fresh surfactant solution was flowed into the cell to flush out about 50 ml of the emulsion once per day to measure the oil content in the emulsion. About 26 PVs of fresh surfactant solution was injected over 44 days. During surfactant imbibition, no oil droplets or blobs with sizes large enough to detect with the naked eye appeared on the surfaces of the core. All of the produced oil was in the form of emulsion.

Figure 4.72: Oil was produced as emulsion.

The oil recovery and oil saturation versus time are shown in Figure 4.73. The final oil recovery after 44 days was 51% OOIP and the final oil saturation was 0.48. The experiment was stopped to measure the permeability of the core. The brine permeability of the core was 14 md. The final oil recovery determined from weighing the core after 44 days of surfactant imbibition was 46% OOIP, which is in good agreement with the value based on the emulsion density.

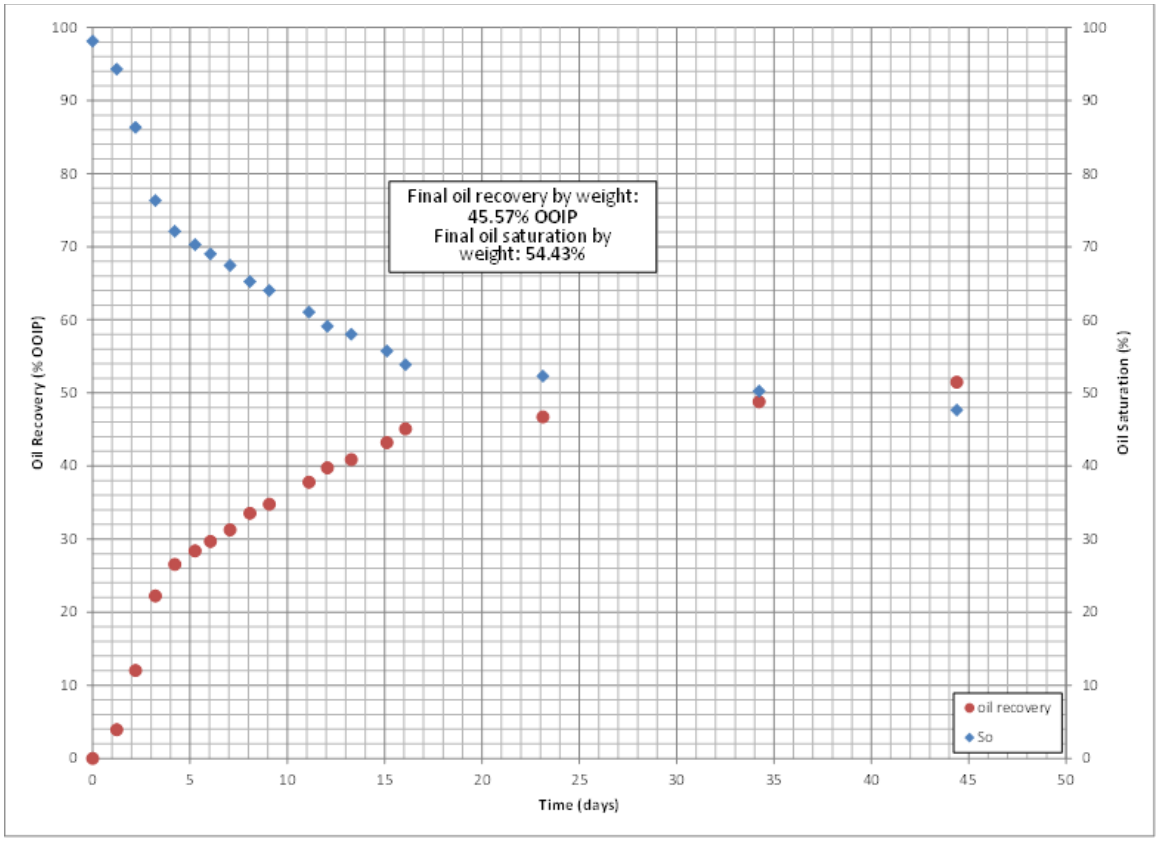


Figure 4.73: Experiment IE 40 oil recovery and oil saturation versus time.

Experiment IE 41

A 3.76 cm diameter by 9.32 cm height (length) Texas cream limestone outcrop core was used for experiment IE 41. To prepare for imbibition, the core was initially fully vacuum-saturated with SAMA surrogate oil (diluted with 10 wt% toluene) at 23 ºC. The core was then aged in SAMA surrogate oil at 78 ºC for 45 days. After preparation, the core was first immersed in 20,000 ppm NaCl brine inside the imbibition cell at 78 °C to observe oil recovery. About 1.5 ml of oil was recovered after 30 hours of brine imbibition.

After brine imbibition, the core was immersed in an aqueous solution of 0.5 wt% C28-25PO-45EO-COO-, 0.2 wt% C15-18-IOS, 0.3 wt% C19-28-IOS, and 1 wt% EDTA

and at 78 ºC. The salinity of the surfactant solution was 20,000 ppm TDS, which was a Winsor Type I salinity. The produced oil was in the form of free oil. Fresh surfactant solution was flowed into the cell to flush out the produced free oil. About 13 PVs of fresh surfactant solution was injected over 41 days.

The oil recovery and oil saturation versus time are shown in Figure 4.74. The final oil recovery after 41 days was 51% OOIP and the final oil saturation was 0.47. The experiment was stopped to measure the permeability of the core. The brine permeability of the core was 41 md. The final oil recovery determined from weighing the core after 41 days of surfactant imbibition was 25% OOIP, which differs significantly from the value based on the emulsion density.

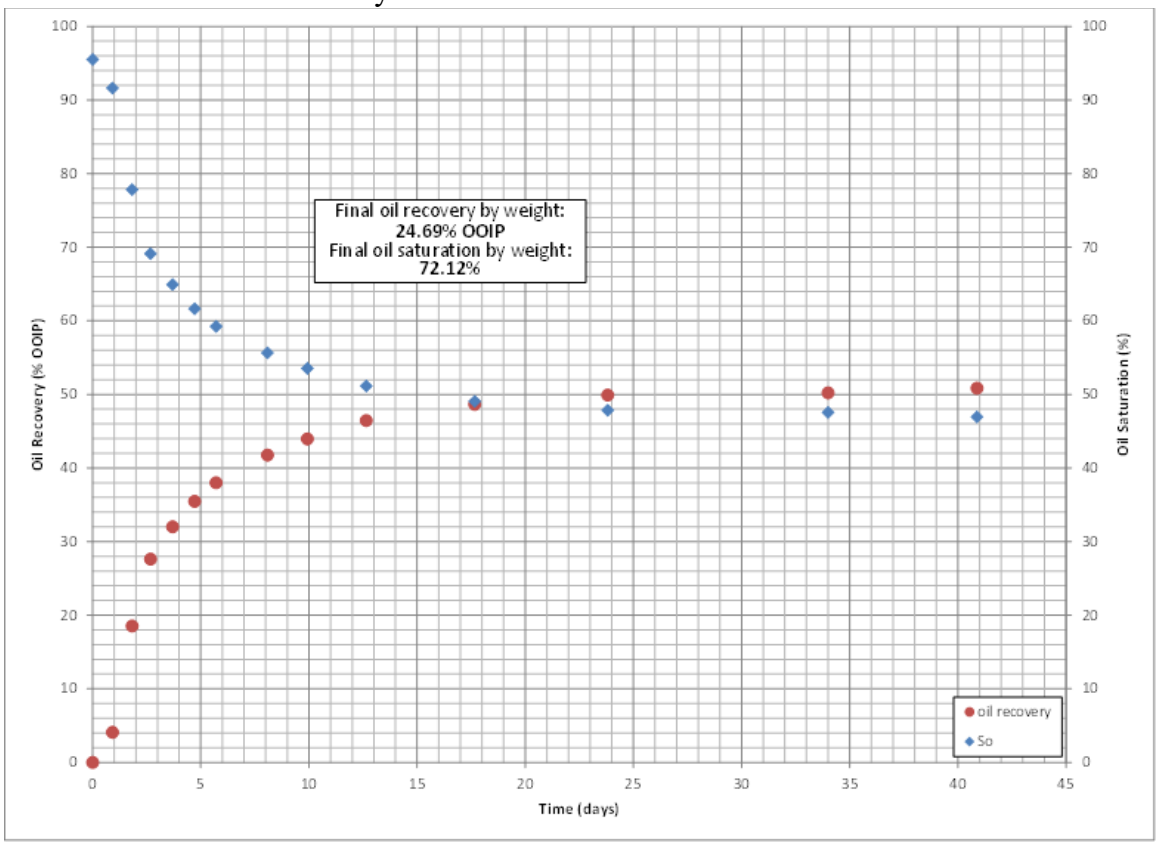


Figure 4.74: Experiment IE 41 oil recovery and oil saturation versus time.

Experiment IE 42

A 3.76 cm diameter by 9.66 cm height (length) Texas cream limestone outcrop core was used for experiment IE 42. To prepare for imbibition, the core was initially fully vacuum-saturated with SAMA surrogate oil (diluted with 10 wt% toluene) at 23 ºC. The core was then aged in SAMA surrogate oil at 78 ºC for 42 days. After preparation, the core was first immersed in 75,000 ppm NaCl brine inside the imbibition cell at 78 °C to observe oil recovery. About 4.1 ml of oil was recovered after 20 hours of brine imbibition. Figure 4.75 shows a photograph of the core after 20 hours of brine imbibition.

Figure 4.75: Experiment IE 42 produced 4.1 ml of oil after 20 hours of brine imbibition.

After brine imbibition, the core was immersed in an aqueous solution of 0.5 wt% C28-25PO-45EO-COO-, 0.2 wt% C15-18-IOS, 0.3 wt% C19-28-IOS, and 0 wt% EDTA and at 78 ºC. The salinity of the surfactant solution was 75,000 ppm TDS, which was the optimal salinity. The oil was produced in the form of an emulsion, causing the color of the liquid surrounding the core to gradually change from clear to dark as shown in Figure 4.76. About 50 ml of fresh surfactant solution was flowed into the cell to flush out about 50 ml of the emulsion once per day to measure the oil content in the emulsion. About 24

PVs of fresh surfactant solution was injected over 44 days. During surfactant imbibition, no oil droplets or blobs with sizes large enough to detect with the naked eye appeared on the surfaces of the core. All of the produced oil was in the form of emulsion.

Figure 4.76: Oil was produced as emulsion.

The oil recovery and oil saturation versus time are shown in Figure 4.77. The final oil recovery after 44 days was 37% OOIP and the final oil saturation was 0.55. The experiment was stopped to measure the permeability of the core. The brine permeability of the core was 54 md. The final oil recovery determined from weighing the core after 44 days of surfactant imbibition was 49% OOIP, which differs from the value based on the emulsion density.

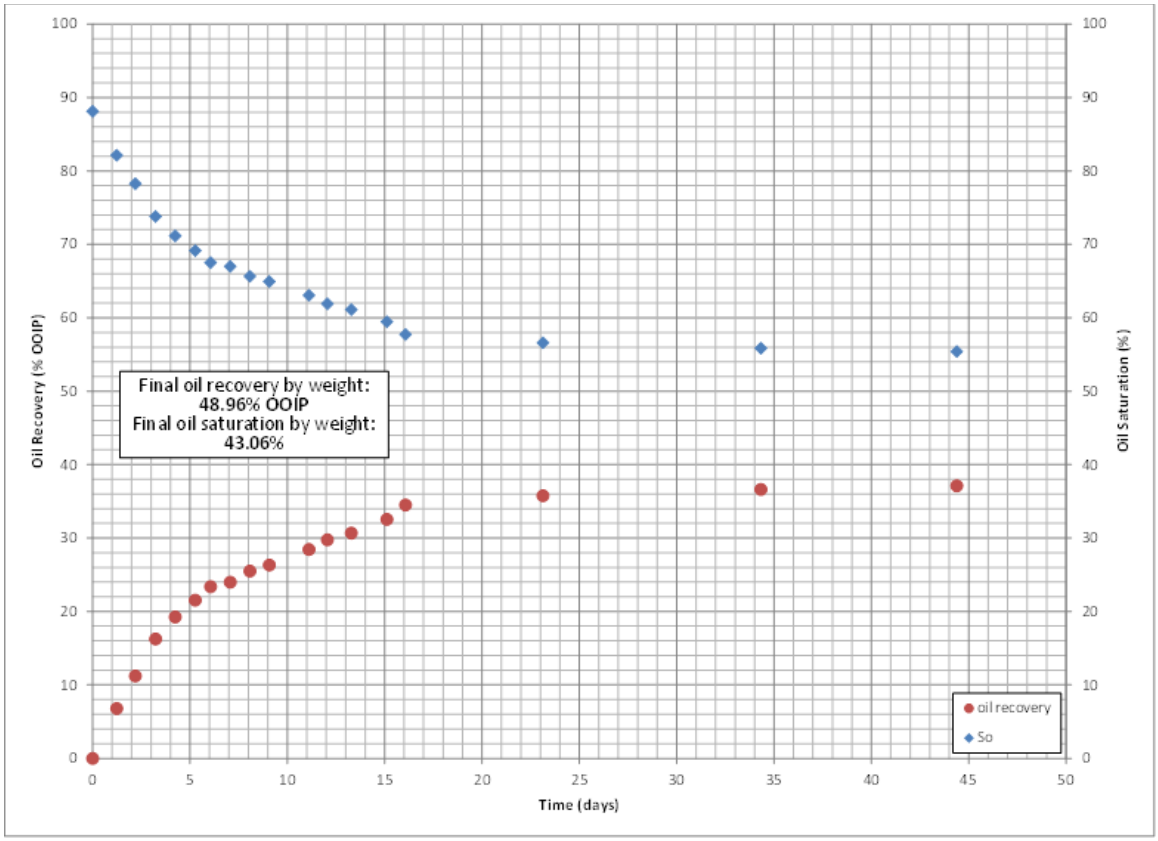


Figure 4.77: Experiment IE 42 oil recovery and oil saturation versus time.

Experiment IE 43

A 3.76 cm diameter by 9.77 cm height (length) Texas cream limestone outcrop core was used for experiment IE 43. To prepare for imbibition, the core was initially fully vacuum-saturated with SAMA surrogate oil (diluted with 10 wt% toluene) at 23 ºC. The core was then aged in SAMA surrogate oil at 78 ºC for 45 days. After preparation, the core was first immersed in 20,000 ppm NaCl brine inside the imbibition cell at 78 °C to observe oil recovery. About 2.6 ml of oil was recovered after 31 hours of brine imbibition.

After brine imbibition, the core was immersed in an aqueous solution of 0.5 wt% C28-25PO-45EO-COO-, 0.2 wt% C15-18-IOS, 0.3 wt% C19-28-IOS, and 0 wt% EDTA

and at 78 ºC. The salinity of the surfactant solution was 20,000 ppm TDS, which was a Winsor Type I salinity. The produced oil was in the form of free oil. Fresh surfactant solution was flowed into the cell to flush out the produced free oil. About 13 PVs of fresh surfactant solution was injected over 41 days.

The oil recovery and oil saturation versus time are shown in Figure 4.78. The final oil recovery after 41 days was 48% OOIP and the final oil saturation was 0.48. The permeability of the core was not measured. The final oil recovery determined from weighing the core after 41 days of surfactant imbibition was 51% OOIP, which is in good agreement with the value based on the emulsion density.

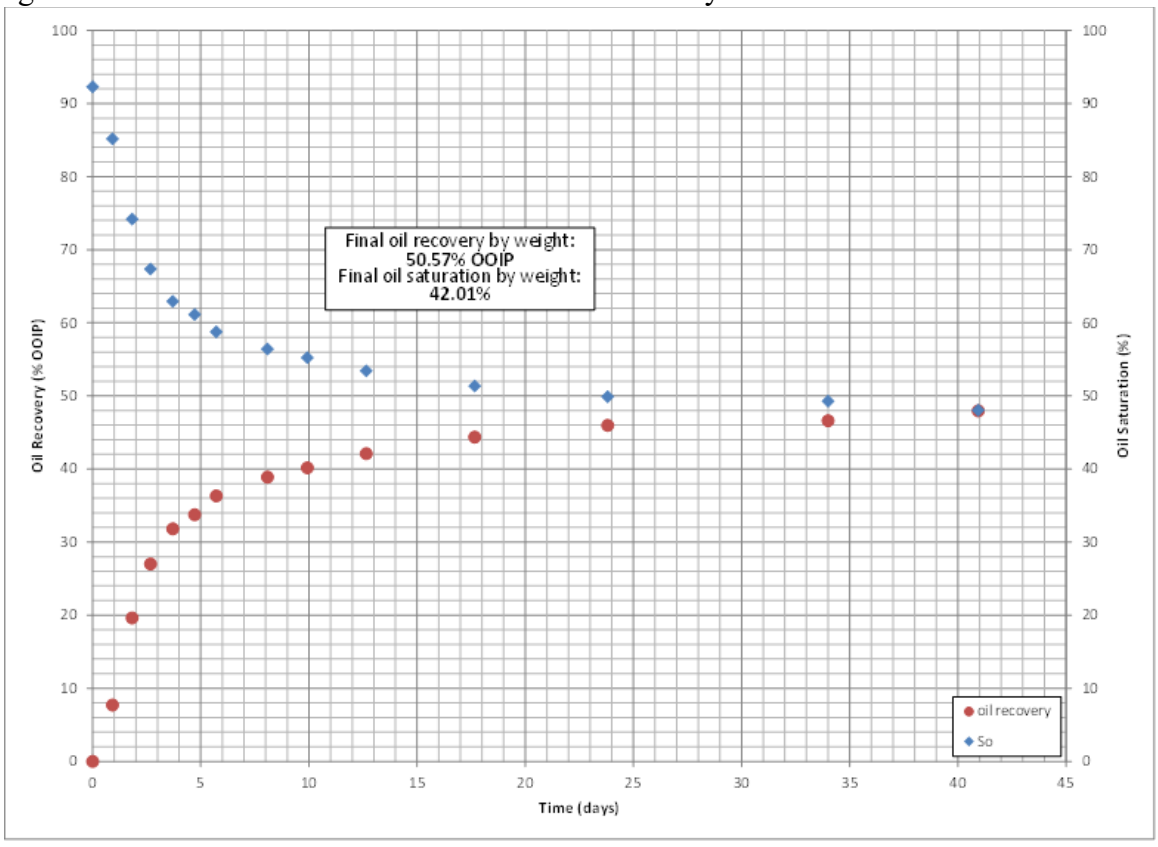


Figure 4.78: Experiment IE 43 oil recovery and oil saturation versus time.

Comparison of Final Oil Recovery from Density Measurement with Final Oil Recovery from Mass Measurement

The cores were weighed after completion of the experiment and the difference between the initial and final mass was used to determine the final oil recovery. This value was compared to the final oil recovery determined using the method described in section 3.5 Method to Measure Oil Production. Table 4.3 shows the comparison of final oil recovery from density measurement with values from mass measurement. The mean of the differences in the final oil recovery was 9% OOIP.

Table 4.3: Comparison of Final Oil Recovery from Density Measurement with Values from Mass Measurement

Experiment IE #	Final Oil Recovery from Density Measurement % OOIP	Final Oil Recovery from Mass Measurement % OOIP	Difference in Final Oil Recovery % OOIP
17	45	45	0
18	38	35	3
19	93	97	-4
21	58	26	32
22	24	23	1
23	47	39	8
24	56	30	26
25	76	81	-5
26	54	55	-1
28	51	55	-4
29	61	67	-6
30	133	78	55
31	80	57	23
32	63	64	-1
33	65	77	-12
34	85	85	0
35	41	49	-8
36	84	15	69
37	121	30	91
40	51	46	5
41	51	25	26
42	37	49	-12
43	48	51	-3
44	34	36	-2
45	39	50	-11
46	42	49	-7
47	38	*	*
48	30	40	-10
49	36	41	-5

*Value not reliable.

The oil recovery based on the final mass measurement was considered to be more accurate than the oil recovery based on the density measurement because the density of numerous small samples had to be measured in each experiment. Therefore, the oil recovery data from density measurement were adjusted by multiplying by the ratio of the final oil recovery from mass measurement to the final oil recovery from density measurement. The adjusted oil recovery data were used for comparison and analysis.

The final oil recovery determined from density and mass measurements differed significantly for the experiments conducted at high temperature (IE 30, 36, and 37). For example, the difference in the final oil recovery was 91% OOIP for experiment IE 37 (see Table 4.3). Therefore, in addition to other reasons, only the oil recovery data for experiments using the McElroy oil at low temperature (23°C) were used for comparison and analysis.

4.3 Comparison of Duplicate Experiments

Experiment IE 21, 25, and 49

Figure 4.79 shows the oil recovery versus time for the duplicate experiments IE 21, 25, and 49. These experiments used Texas cream limestone cores with dimensions of about 3.8 cm diameter by 10 cm height and surfactant formulation 2 at optimal salinity. Both IE 21 and 49 had a permeability of about 7 md. The oil recovery was nearly the same until 28 days and only slightly different after 28 days. The permeability of IE 25 was 47 md, about 7 times higher than that of IE 21 and 49. The oil recovery of IE 25 was much higher than that of IE 21 and 49. At 64 days, the oil recovery for IE 25 is nearly 2 times higher than for IE 21 and 49. As shown in the next chapter, oil recovery scales with the square root of permeability. The square root of the permeability ratio is 2.6. Thus,

most of the difference in the oil recovery can be explained by the large contrast in the permeability.

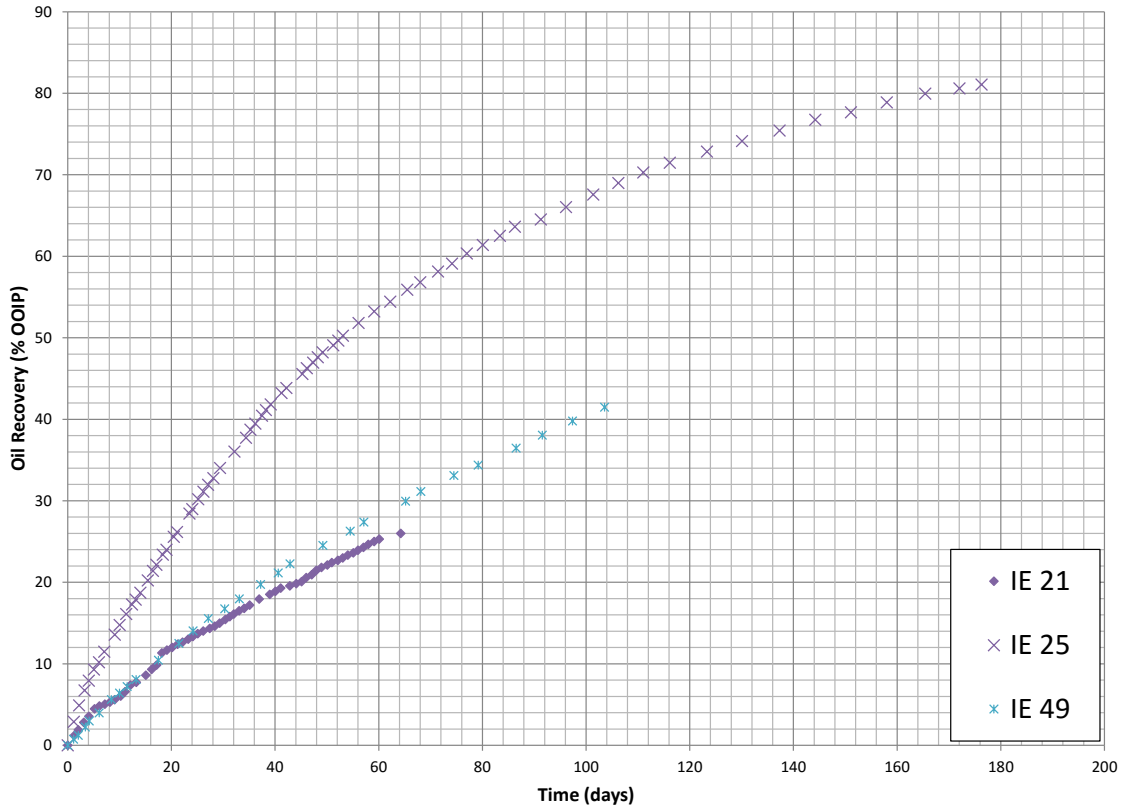


Figure 4.79: Oil recovery versus time for the duplicate experiments IE 21, 25, and 49.

Experiment IE 31 and 34

Figure 4.80 shows the oil recovery versus time for the duplicate experiments IE 31 and 34. These experiments used Texas cream limestone cores with dimensions of about 3.8 cm diameter by 10 cm height and surfactant formulation 7 at optimal salinity. The permeability of IE 34 was about 2 times higher than that of IE 31. The square root of the permeability ratio is 1.41. The final oil recovery of IE 34 was about 1.49 times higher than that of IE 31. The final oil recovery of IE 34 divided by 1.41 is 60.3% OOIP compared to 57% OOIP for IE 31 or a difference of 3% OOIP. Thus, most of the

difference in oil recovery can be explained by the difference in permeability between the two cores.

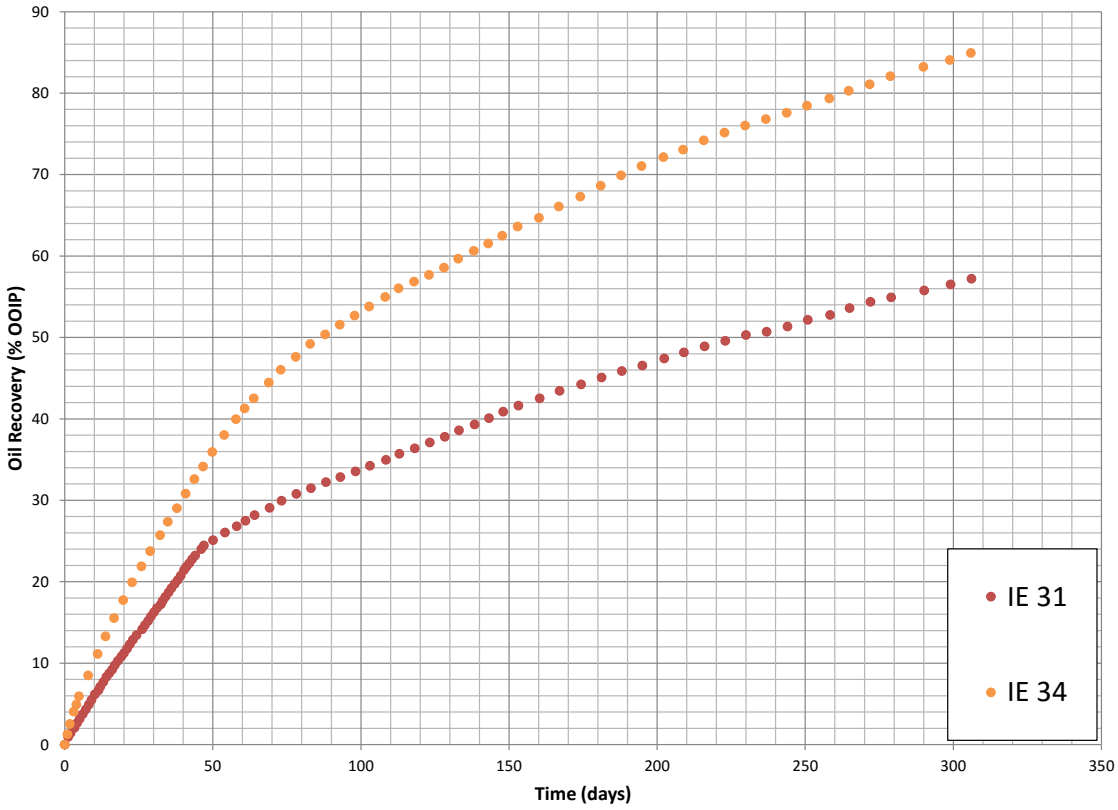


Figure 4.80: Oil recovery versus time for the duplicate experiments IE 31 and 34.

Experiment IE 22 and 26

Figure 4.81 shows the oil recovery versus time for the duplicate experiments IE 22 and 26. These experiments used Texas cream limestone cores with dimensions of about 10.8 cm diameter by 9.4 cm height and surfactant formulation 2 at optimal salinity. The permeability of both IE 22 and 26 was about 7 md. The final oil recovery for IE 22 was about 23% OOIP and for IE 26 it was about 17% OOIP. The difference between the two recoveries is thus 5% OOIP.

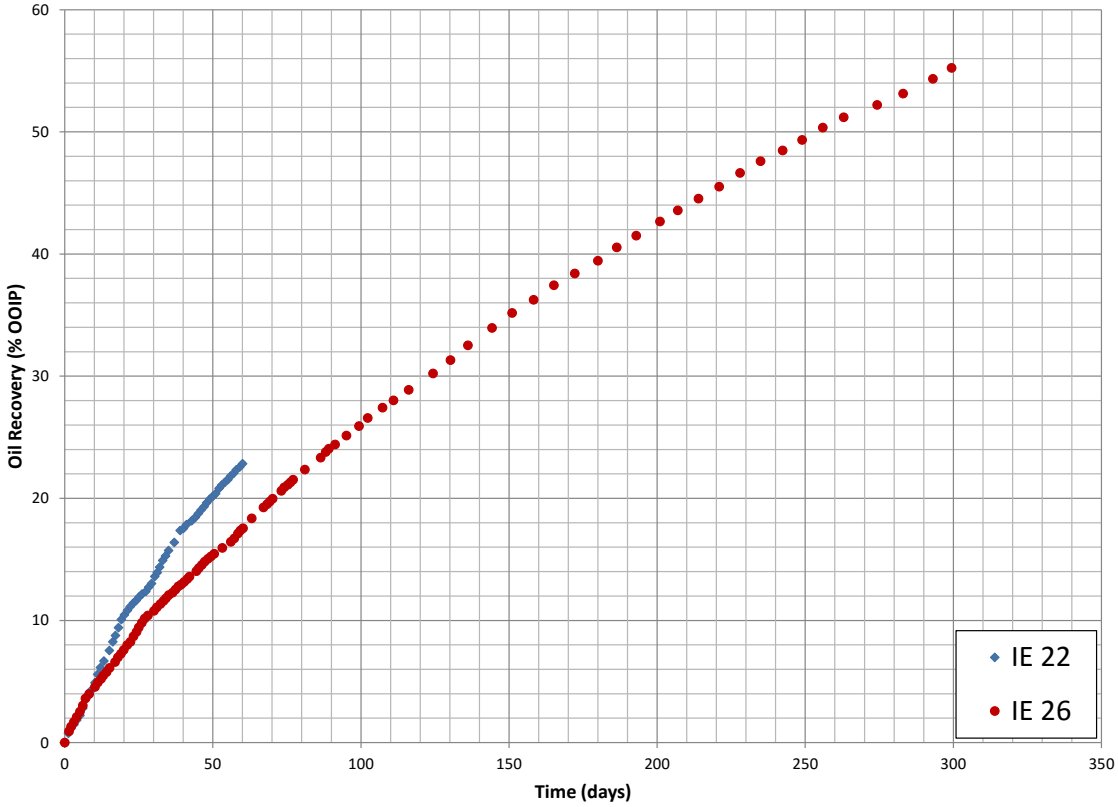


Figure 4.81: Oil recovery versus time for the duplicate experiments IE 22 and 26.

Experiment IE 29 and 45

Figure 4.82 shows the oil recovery versus time for the duplicate experiments IE 29 and 45. These experiments used Texas cream limestone cores with dimensions of about 3.8 cm diameter by 30 cm height and surfactant formulation 2 at optimal salinity. The permeability of IE 29 was about 2 times higher than that of IE 45. The difference in oil recovery after adjusting for the difference in permeability between the two cores is about 5% OOIP. Thus, it would appear that the experiments can be reproduced within a difference of about 5% OOIP. This difference of 5% OOIP is due to uncertainties in the measurements but also some of it is likely due to other unknown differences in the cores.

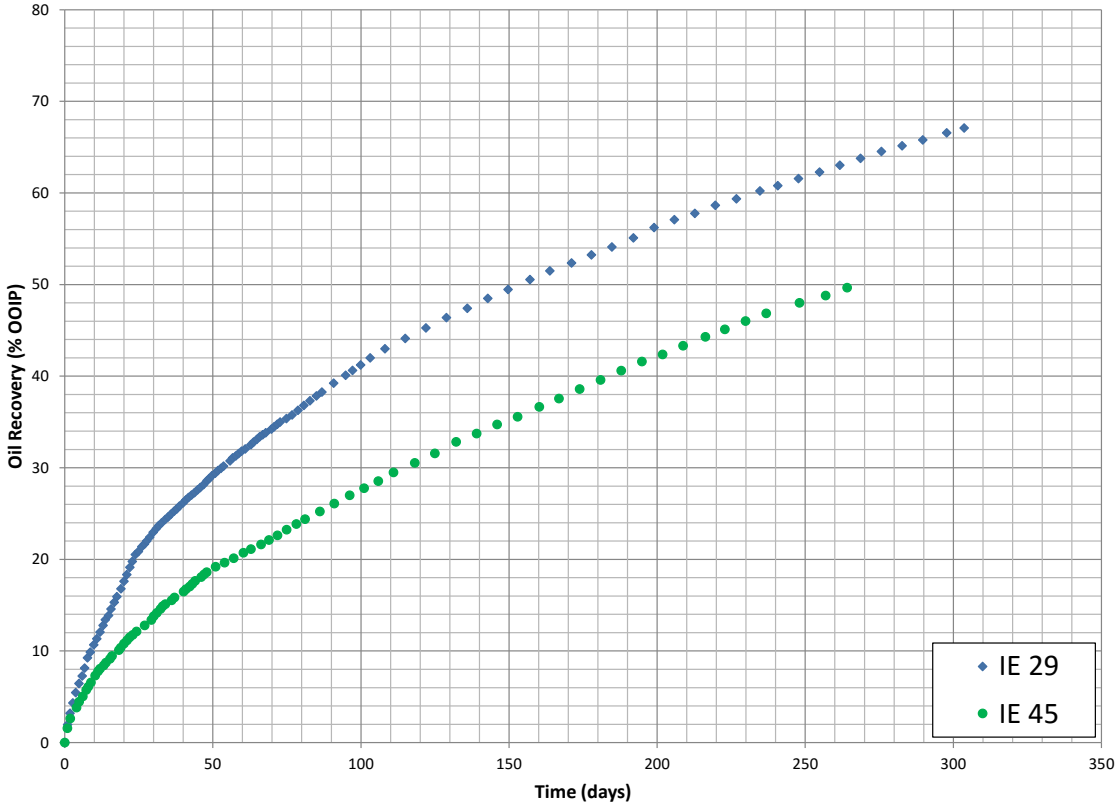


Figure 4.82: Oil recovery versus time for the duplicate experiments IE 29 and 45.

4.4 Comparison of Experiments with Different Parameters

4.4.1 Horizontal Length

Figure 4.83 shows a comparison of the oil recovery data for cores of 3.8, 10, and 20 cm horizontal lengths by constant 10 cm height. These experiments used Texas cream limestone cores and surfactant formulation 2 at optimal salinity. Taking into account the differences in permeability, the results show that for cores of 10 cm height oil recovery decreases as horizontal length increases.

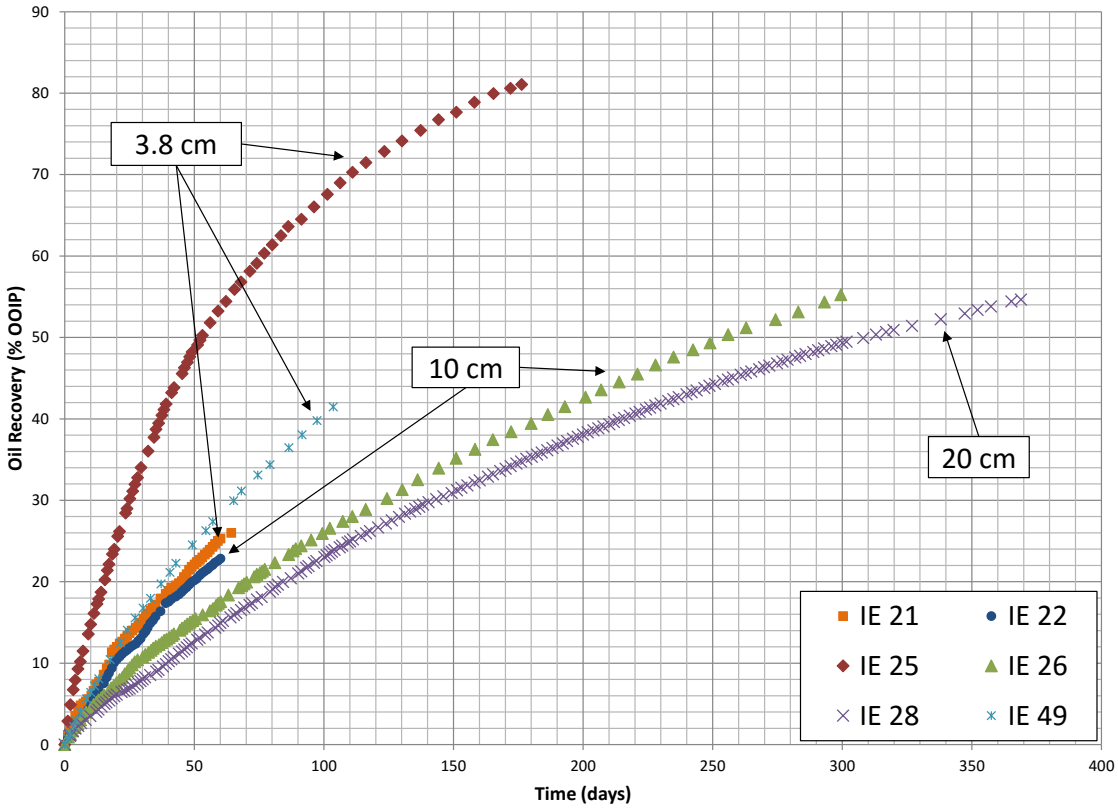


Figure 4.83: Oil recovery versus time for cores of 3.8, 10, and 20 cm horizontal lengths by constant 10 cm height.

Figure 4.84 shows a comparison of the oil recovery data for cores of 3.8 and 10 cm diameters by constant 30 cm height. These experiments used Texas cream limestone cores and surfactant formulation 2 at optimal salinity. Taking into account the differences in permeability, the results show that for cores of 30 cm height oil recovery decreases as horizontal length increases.

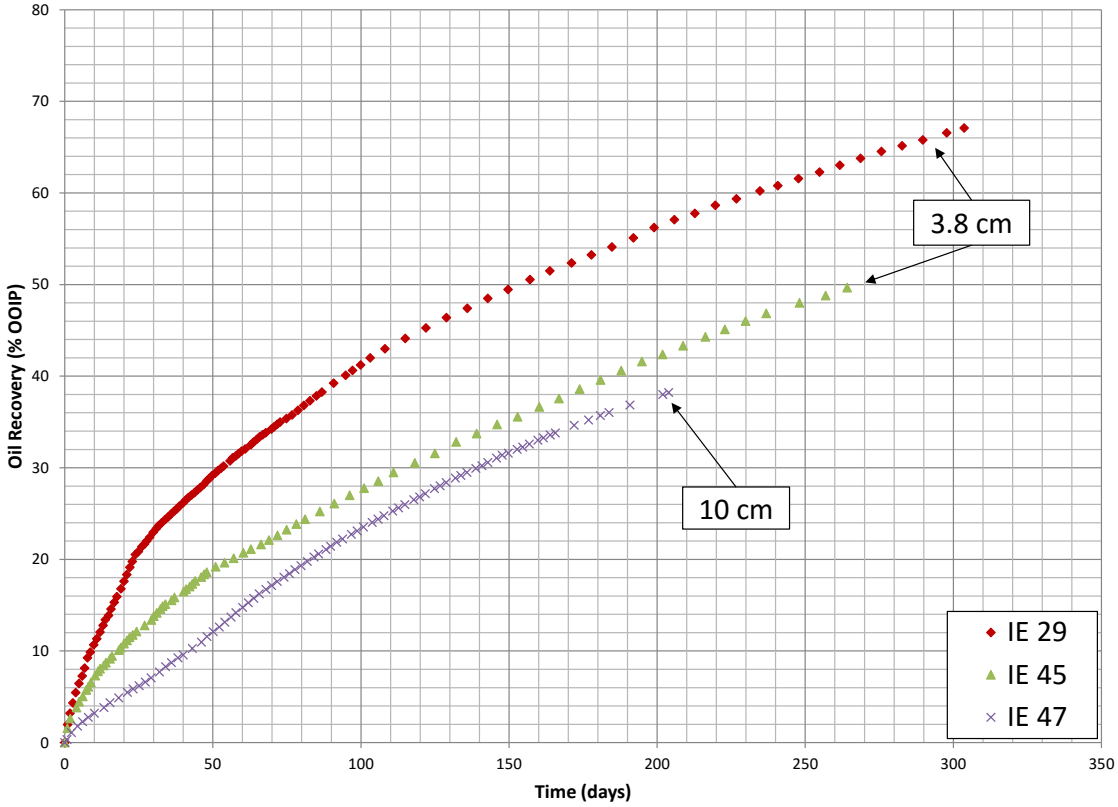


Figure 4.84: Oil recovery versus time for cores of 3.8 and 10 cm diameters by constant 30 cm height.

4.4.2 Vertical Length

Figure 4.85 shows a comparison of the oil recovery data for cores of 10 and 30 cm heights by constant 3.8 cm diameter. These experiments used Texas cream limestone cores and surfactant formulation 2 at optimal salinity. Taking into account the differences in permeability, the results show that for cores of 3.8 cm diameter oil recovery is lower for cores with a larger vertical length or height.

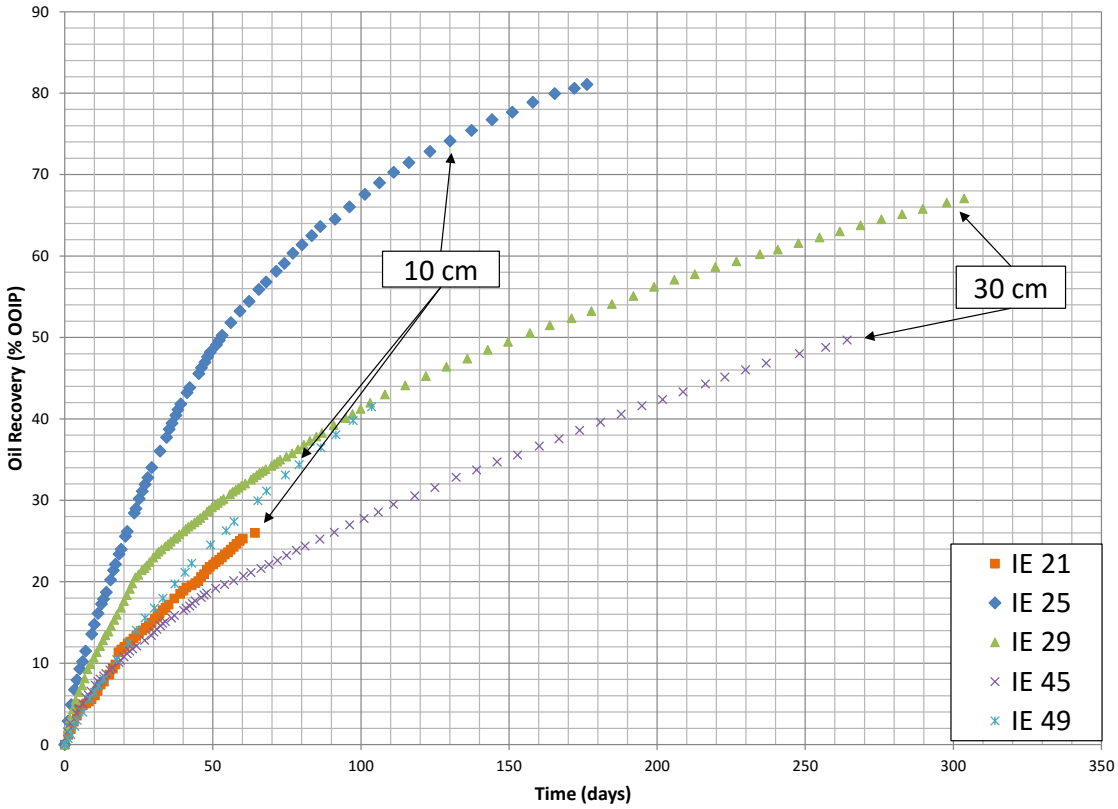


Figure 4.85: Oil recovery versus time for cores of 10 and 30 cm heights by constant 3.8 cm diameter.

Figure 4.86 shows a comparison of the oil recovery data for cores of 10 and 30 cm heights by constant 10 cm diameter. These experiments used Texas cream limestone cores and surfactant formulation 2 at optimal salinity. Taking into account the differences in permeability, the results show that for cores of 10 cm diameter oil recovery is lower for cores with a larger vertical length or height.

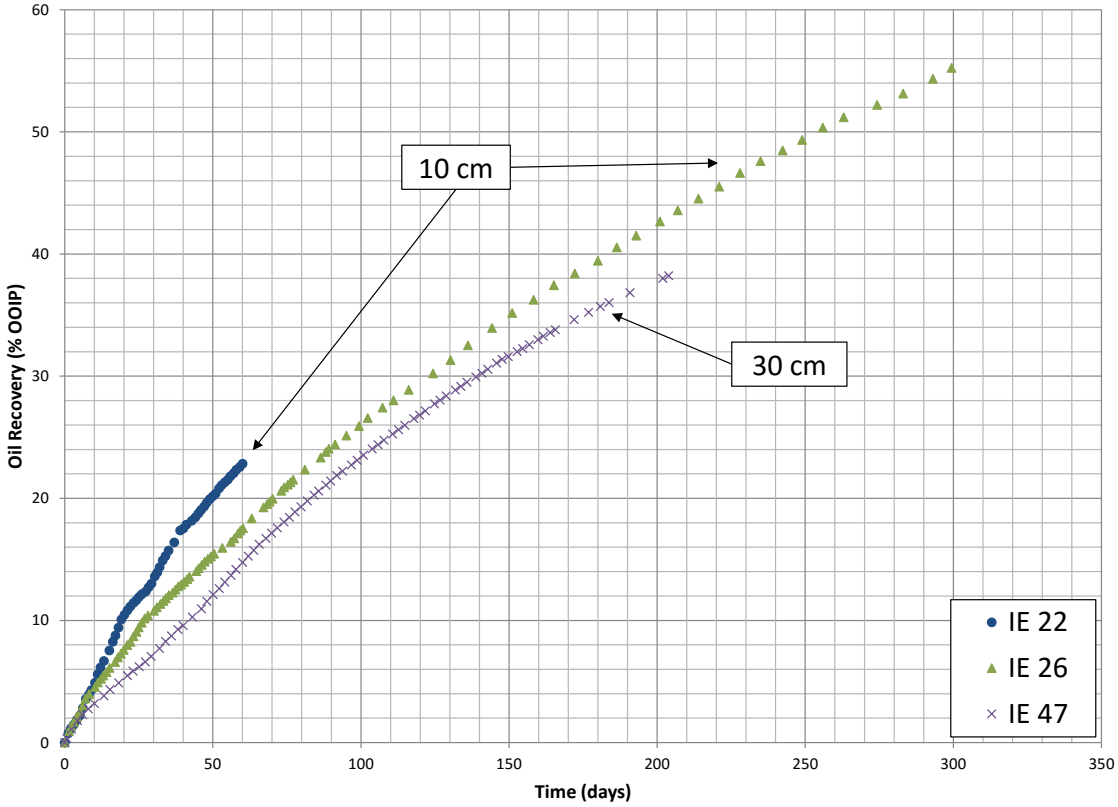


Figure 4.86: Oil recovery versus time for cores of 10 and 30 cm heights by constant 10 cm diameter.

4.4.3 Permeability

Figure 4.87 shows a comparison of the oil recovery data for Silurian dolomite and Texas cream limestone cores of different permeability. The permeability of the Silurian dolomite core (IE 19) was 58 md, and the permeability of the Texas cream limestone cores (IE 25 and 49) were 47 and 8 md, respectively. These experiments used cores with dimensions of about 3.8 cm diameter by 10 cm height and surfactant formulation 2 at optimal salinity. The results show that oil recovery is higher for cores with a larger permeability.

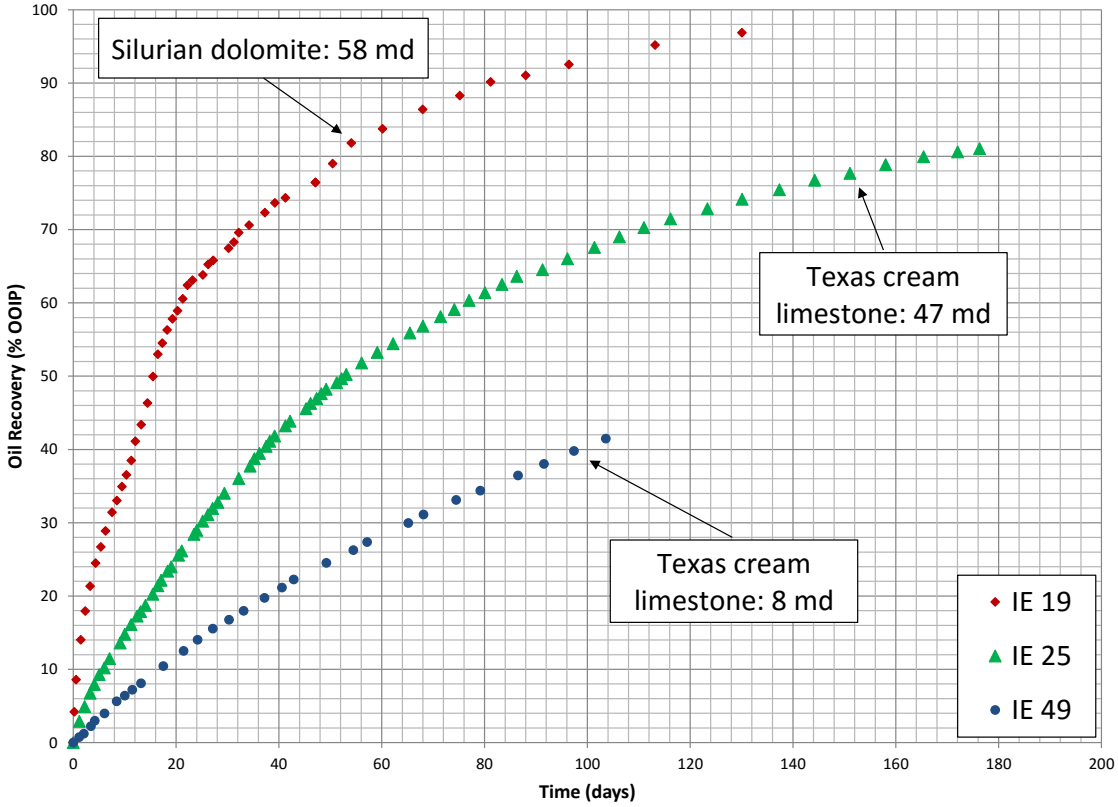


Figure 4.87: Oil recovery versus time for Silurian dolomite and Texas cream limestone cores of different permeability.

4.4.4 IFT

Figure 4.88 shows a comparison of the oil recovery data for experiments with different IFTs. These experiments used Texas cream limestone cores with dimensions of about 3.8 cm diameter by 10 cm height and surfactant formulation 2. The IFT was varied by changing the salinity of the surfactant solution. The solubilization ratios were measured with a salinity scan (Figure 4.2) and used to estimate the IFTs of 0.002, 0.03, and 0.3 dynes/cm for experiments IE 21/25/49, 33, and 46 respectively using the Huh's equation (Huh 1979). The experiment with the highest IFT showed the lowest oil

recovery, but the dependence was very weak over this range of IFT since the capillary pressure was small even at the highest IFT.

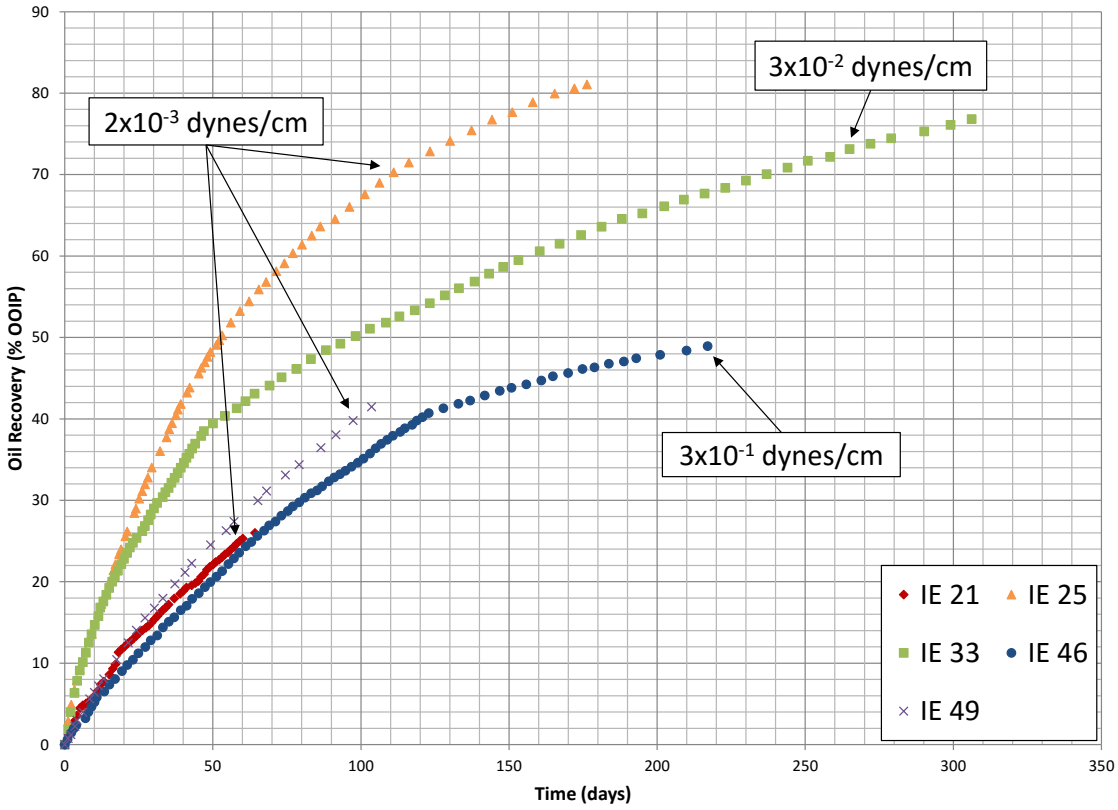


Figure 4.88: Oil recovery versus time for experiments with IFTs of 0.002, 0.03, and 0.3 dynes/cm.

4.4.5 Surfactant and Co-Solvent Concentrations

Figure 4.89 shows a comparison of the oil recovery data for experiments using three surfactant formulations with different surfactant concentrations. The surfactant formulations 5, 6, and 2 were used. The surfactant concentrations were 0.25, 0.5, and 1.0 wt%. These experiments used Texas cream limestone cores with dimensions of about 3.8 cm diameter by 10 cm height and the same surfactants and co-solvents. For each experiment, the ratio of surfactant concentration to co-solvent concentration was 1:1.

Taking into account the differences in permeability, the results show that oil recovery is higher for experiments using a higher surfactant concentration.

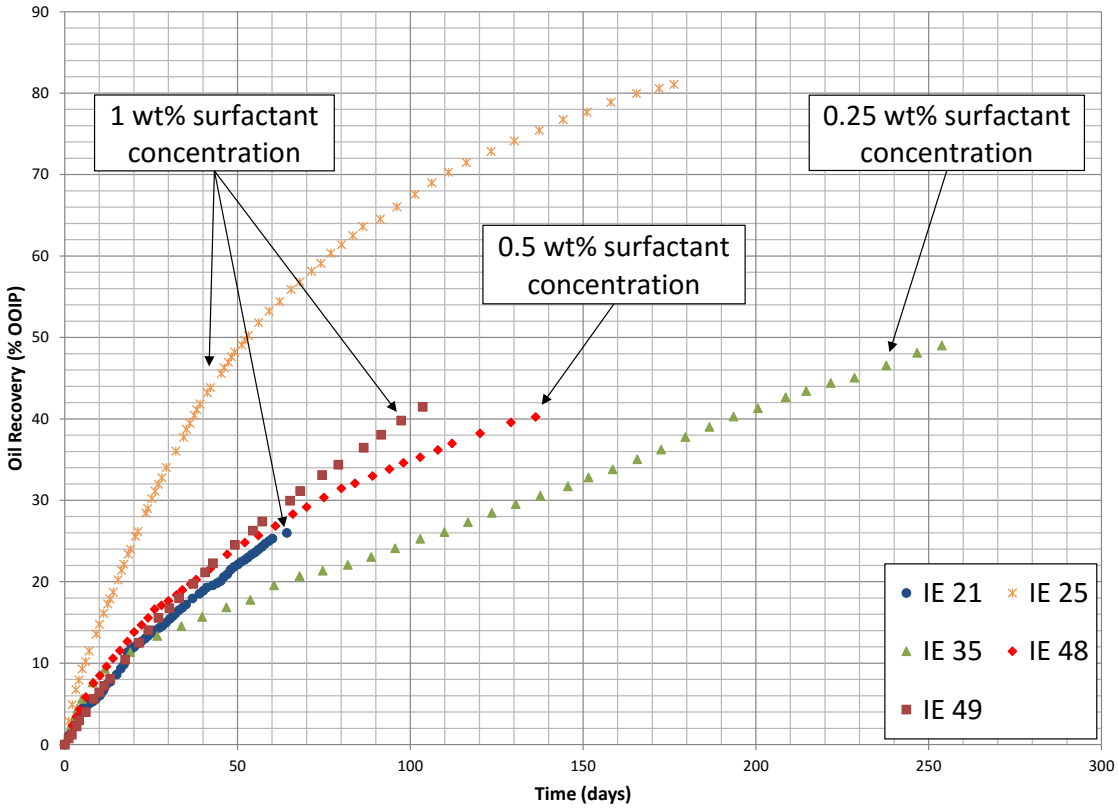


Figure 4.89: Oil recovery versus time for experiments using 0.25, 0.5, and 1.0 wt% surfactant concentrations.

Figure 4.90 shows a comparison of the oil recovery data for experiments using three surfactant formulations with different co-solvent concentrations. The surfactant formulations 3, 2, and 4 were used. The co-solvent concentrations were 0, 1.0, and 2.0 wt%. These experiments used Texas cream limestone cores with dimensions of about 3.8 cm diameter by 10 cm height and the same surfactants and co-solvents. The experiments using higher co-solvent concentrations of 1.0 and 2.0 wt% had higher oil recovery. The experiment without using any co-solvent had the lowest oil recovery. A possible

explanation is that the surfactant formulations with co-solvent reduced the microemulsion viscosity and therefore increased the rate of imbibition and oil recovery.

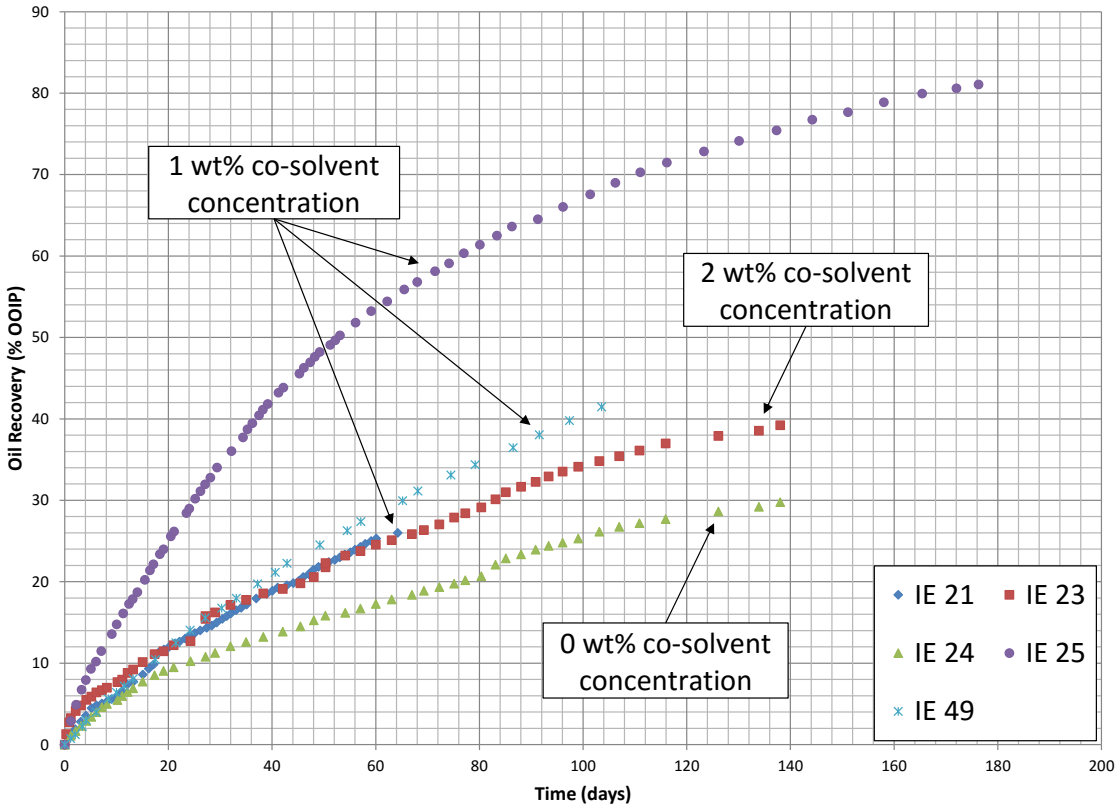


Figure 4.90: Oil recovery versus time for experiments using 0, 1.0, and 2.0 wt% co-solvent concentrations.

Chapter 5: Comparison of Experimental Results with New Imbibition Model

5.1 Overview of Model and Scaling

The purpose of this chapter is to analyze the experimental oil recovery data by comparing it with a new analytical model for the imbibition process (Li et al. 2016; Pope 2016) and to test the model with respect to core dimensions and other parameters affecting the oil recovery. The derivation of the analytical model for both cylindrical and rectangular geometries is shown in Appendix A.

The analytical model predicts the oil recovery as a function of time for low IFT surfactant imbibition. Under low IFT conditions, buoyancy causes a mostly horizontal flow of the invading surfactant solution and a mostly vertical flow of the microemulsion. Both of the horizontal and vertical flow results in small pressure gradients that must be taken into account to understand how the oil recovery scales with length. Larger diameters (or horizontal lengths) result in a greater horizontal pressure drop and slower oil recovery. Core height affects the flow in a more complicated way since a greater vertical distance increases both the buoyancy and the vertical pressure drop as shown in Appendix A.

The oil recovery as a fraction of the initial oil in place is expressed as follows:

$$\frac{\Delta V_o}{V_{oi}} = \frac{r_b}{R} - \frac{1}{3}\left(\frac{r_b}{R}\right)^2$$

where

$$\frac{r_b}{R} = \sqrt{\frac{2k_w k_{rw} \Delta\rho g H t}{\mu_w \phi (1 - S_{orc} + D_s)(R^2 + MH^2)}}$$

and

$$M = \frac{k_{rw}\mu_o}{k_{ro}\mu_w}$$

The oil recovery factor as a function of non-dimensional time can be expressed as follows:

$$\frac{\Delta V_o}{V_{oi}} = \sqrt{t_d} - \frac{t_d}{3}$$

where the non-dimensional time is defined as follows:

$$t_d = \frac{2k_w k_{rw} \Delta\rho g H t}{\phi \mu_w (R^2 + MH^2)}$$

S_{orc} has been assumed to be zero in these equations (see Appendix A for more general case).

An analogous result for rectangular blocks is given in Appendix A. The result is the same if R is replaced by $\frac{L}{2}$ where L is the horizontal length of the rock matrix. The model implies that at early time the oil recovery will scale as the square root of L_c defined as follows:

$$L_c = \begin{cases} \dfrac{H}{\left(\frac{L}{2}\right)^2 + MH^2} & rectangular\ block \\ \dfrac{H}{R^2 + MH^2} & cylindrical\ core \end{cases}$$

The scaling derived from this model is similar to the scaling group proposed by Hui et al. (2014). They empirically inferred the following scaling group from a numerical simulation study:

$$L_c = \frac{H}{\left(\frac{L_x}{2}\right)^2 + \left(\frac{L_y}{2}\right)^2 + H^2}$$

The scaling equations are the same for a matrix block with a square base if the mobility ratio is one. The new analytical model is more general since it predicts the dependence on oil viscosity, permeability, porosity, density difference, and as well as horizontal and vertical lengths. The model predicts the oil recovery will decrease as either H or L increases. However, the decrease is not proportional to the increase in either H or L, and also depends on mobility ratio. The mobility ratio varied from about 0.05 to 9.45 for the experiments reported in this thesis and in general it will vary over a wide range in the field, so its effect on the scaling group is very significant.

5.2 Oil Recovery Scaling with Square Root of Permeability and Time

The new analytical model predicts the initial oil recovery is proportional to the square root of permeability and time (see Appendix A). Figure 5.1 to Figure 5.4 show the oil recovery versus square root of permeability times time for the four sets of duplicate experiments shown previously in section 4.3 Comparison of Duplicate Experiments. Permeability is in md, and time is in days. The oil recovery data for all of the duplicate experiments now agree within 4% OOIP with the exception of experiment IE 25 (18% OOIP). Thus, it is reasonable to conclude that the measurement errors for most of the experiments are less than 4% OOIP.

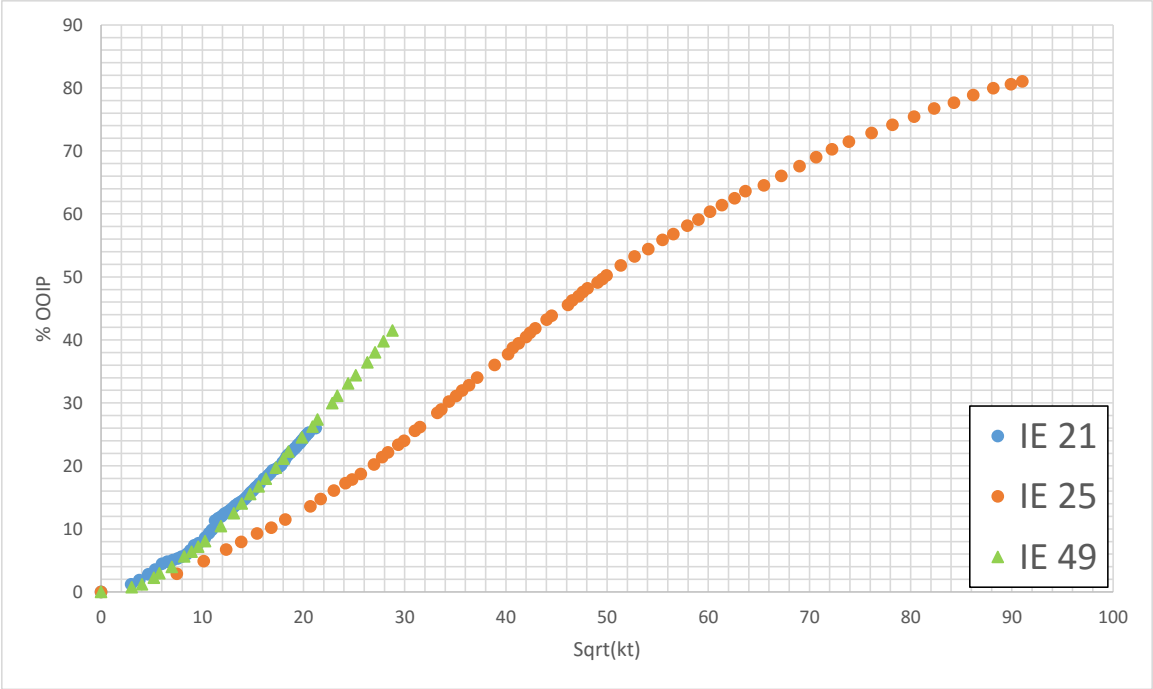


Figure 5.1: Oil recovery versus square root of permeability times time for the duplicate experiments IE 21, 25, and 49.

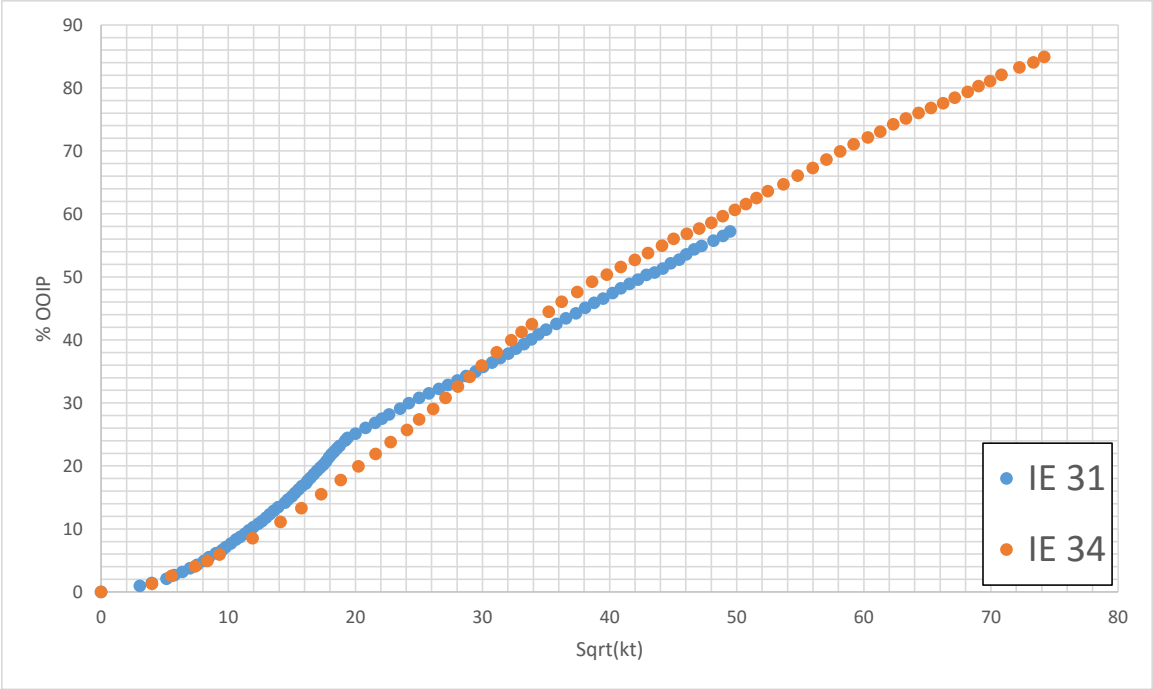


Figure 5.2: Oil recovery versus square root of permeability times time for the duplicate experiments IE 31 and 34.

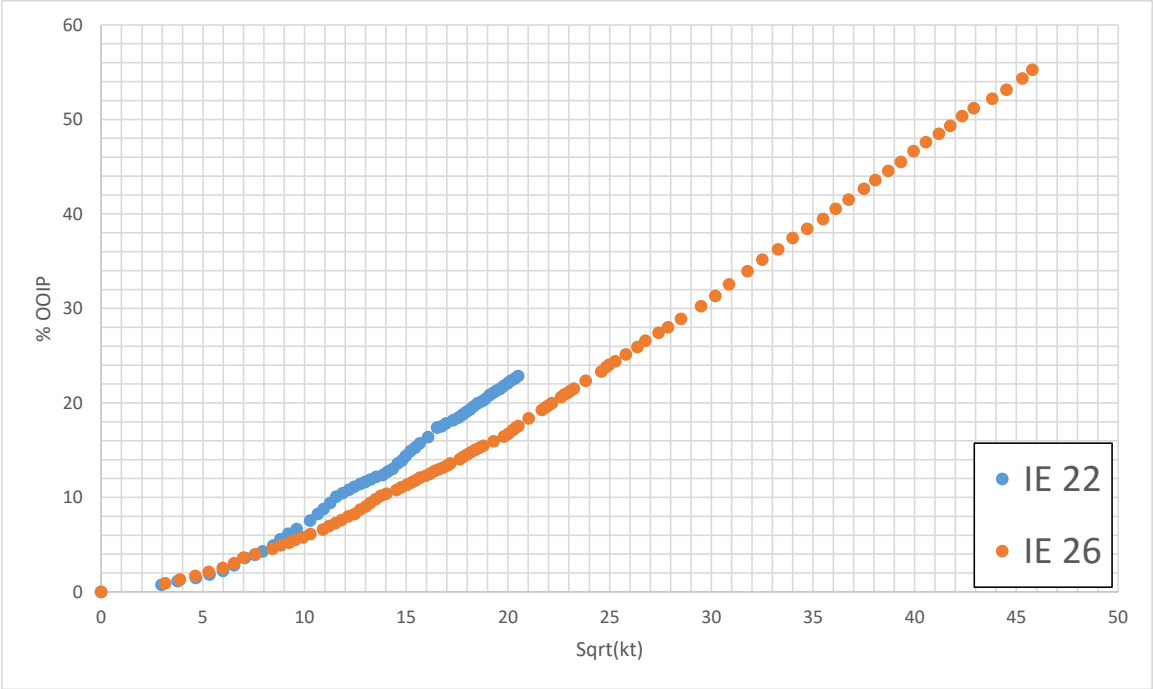


Figure 5.3: Oil recovery versus square root of permeability times time for the duplicate experiments IE 22 and 26.

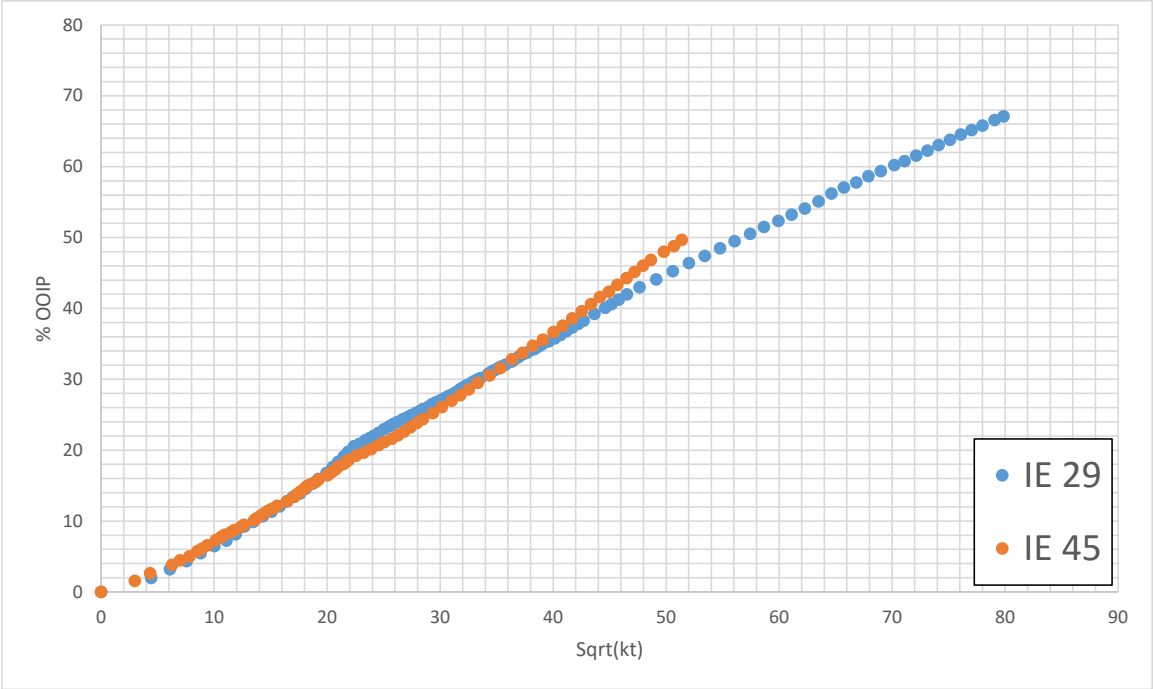


Figure 5.4: Oil recovery versus square root of permeability times time for the duplicate experiments IE 29 and 45.

5.3 Oil Recovery Plotted Using Non-Dimensional Time

Figure 5.5 shows the oil recovery versus time for all of the experiments. Figure 5.6 shows the same data plotted versus the square root of time. As suggested by the model, the data follow a nearly linear tread when plotted versus the square root of time. At early times such as 50 days, the oil recovery is about 6 times higher for the experiment with the highest oil recovery compared with the experiment with the lowest oil recovery. At 100 days, the oil recovery varies by a factor of about 4. Thus, the variation in the oil recovery due to variables such as the core diameter and permeability is much larger than the uncertainty in the data.

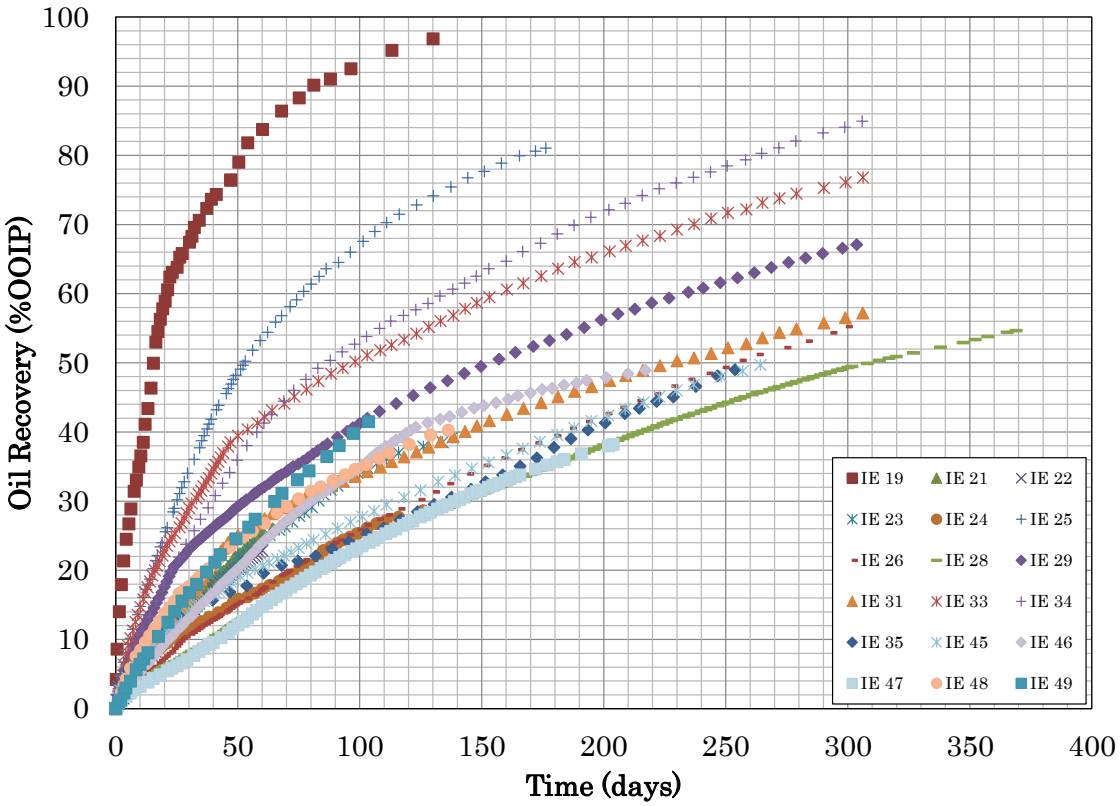


Figure 5.5: Oil recovery versus time for all imbibition experiments.

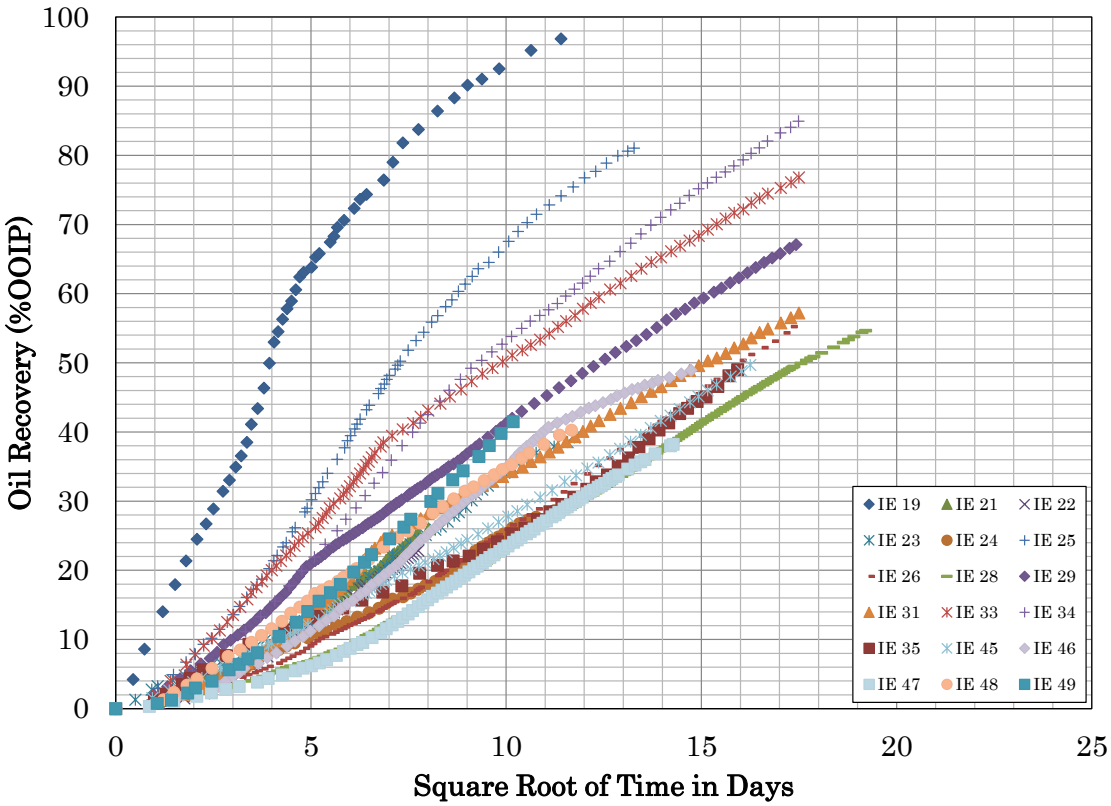


Figure 5.6: Oil recovery versus square root of time for all imbibition experiments.

Figure 5.7 shows a plot of the oil recovery versus the square root of non-dimensional time. The values used to calculate non-dimensional time are shown in Table 5.1. Almost all of the oil recovery data are within a factor of 1.1 of the model curve compared with a total variation of a factor of 6 when plotted versus real time. The only parameter used to fit the experimental data was the microemulsion relative permeability k_{rw}. The ratio of $\frac{k_{rw}}{k_{ro}}$ was fixed at 0.75 in all cases. The value of $S_{orc} + D_s$ was assumed to be zero since the two factors roughly cancel out and neither of these parameters were measured. Remarkably, all but two of the experiments could be approximately matched using $k_{rw} = 0.3$ (see legend in Figure for all k_{rw} values). The experiment with the highest IFT (IE 46) and the experiment with the lowest surfactant

concentration (IE 35) were the exceptions. A better fit was obtained using $k_{rw} = 0.03$ for IE 35 and $k_{rw} = 0.15$ for IE 46.

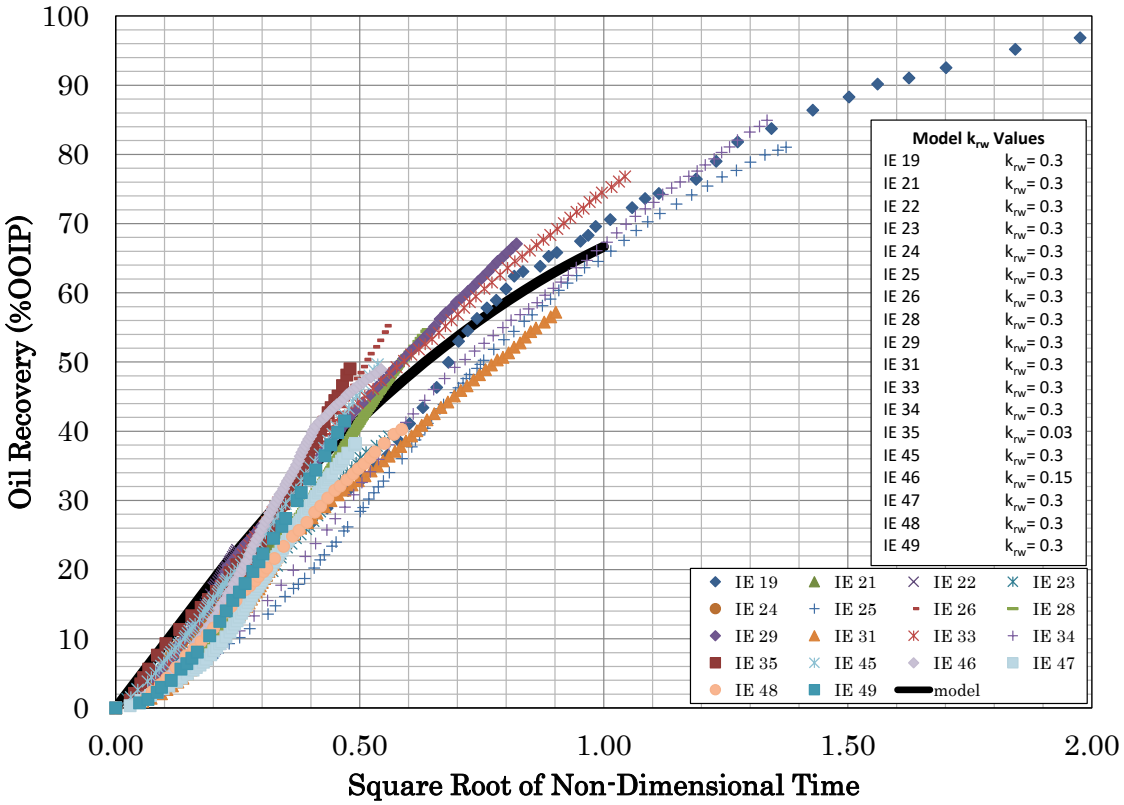


Figure 5.7: Oil recovery versus square root of non-dimensional time for all imbibition experiments.

Table 5.1: Values used to calculate non-dimensional time t_d in Figure 5.7. The microemulsion relative permeability was the only fitting parameter.

Experiment	Diameter	Height	Porosity	Brine Permeability	Density Difference	Microemulsion Viscosity	Oil Viscosity	Microemulsion Relative Perm	Oil Relative Perm	Mobility Ratio
IE #	cm	cm		md	g/ml	cp	cp			
19	3.80	10.00	0.134	58	0.143	45	12.6	0.3	0.4	0.21
21	3.76	9.55	0.278	7	0.157	45	12.6	0.3	0.4	0.21
22	10.80	9.43	0.233	7	0.157	45	12.6	0.3	0.4	0.21
23	3.78	9.42	0.253	8	0.160	45[+]	12.6	0.3	0.4	0.21
24	3.77	9.57	0.246	5	0.146	200[+]	12.6	0.3	0.4	0.05
25	3.77	9.78	0.321	47	0.157	45	12.6	0.3	0.4	0.21
26	10.80	9.35	0.239	7	0.157	45	12.6	0.3	0.4	0.21
28	20.2*	9.50	0.264	26	0.157	45	12.6	0.3	0.4	0.21
29	3.77	29.60	0.264	21	0.157	45	12.6	0.3	0.4	0.21
31	3.77	9.26	0.261	8	0.163	21	12.6	0.3	0.4	0.45
33	3.78	10.03	0.244	11	0.148	1	12.6	0.3	0.4	9.45
34	3.79	10.01	0.251	18	0.163	21	12.6	0.3	0.4	0.45
35	3.77	9.57	0.344	44	0.150	45[+]	12.6	0.03	0.04	0.21
45	3.76	29.40	0.258	10	0.157	45	12.6	0.3	0.4	0.21
46	3.75	9.90	0.245	9	0.137	1	12.6	0.15	0.2	9.45
47	9.80	29.23	0.237	11	0.157	45	12.6	0.3	0.4	0.21
48	3.76	9.86	0.258	9	0.155	45[+]	12.6	0.3	0.4	0.21
49	3.76	9.83	0.276	8	0.157	45	12.6	0.3	0.4	0.21

*Horizontal length of square base.

[+]Value estimated based on the viscosity data of surfactant formulation 2.

5.4 DISCUSSION

A comparison of the experimental oil recovery at a fixed time with the model is shown in Table 5.2. The mean of the differences in the oil recovery is -4% OOIP and the standard error is 5.5% OOIP. The agreement is very good considering the experimental uncertainties and the variations in the experimental conditions: the diameter varied by a factor of 5, the height by a factor of 3, the permeability by a factor of 11, the microemulsion viscosity by a factor of 45, the porosity by a factor of 2, and the IFT by a factor of 100. A value of $k_{rw} = 0.3$ was used to match all of the experiments except the experiment with relatively high IFT and the experiment with low surfactant concentration. A microemulsion relative permeability of 0.3 at low IFT seems reasonable since relative permeability increases as IFT decreases. An even better fit of the data would be possible by adjusting the unknown parameters k_{rw}, S_{orc}, or D_s, but since the

differences between the model and the measured oil recovery data are nearly as low as the experimental uncertainty in the data of about 4% OOIP (based on duplicate experiments), it seems neither necessary nor desirable to attempt further improvement in the fit of the data.

Table 5.2: Comparison of Experimental Oil Recovery After 60 Days with Values Calculated Using Model

Experiment	Experimental Oil Recovery % OOIP	Model Predicted Oil Recovery % OOIP	Difference in Oil Recovery % OOIP
IE 19	70*	67*	3
IE 21	25	30	-5
IE 22	23	23	0
IE 23	25	32	-7
IE 24	17	21	-4
IE 25	53	59	-6
IE 26	18	23	-5
IE 28	15	24	-9
IE 29	32	32	0
IE 31	27	35	-8
IE 33	42	39	3
IE 34	41	47	-6
IE 35	19	22	-3
IE 45	21	23	-2
IE 46	24	26	-2
IE 47	15	24	-9
IE 48	27	34	-7
IE 49	28	31	-3

*Value at 33 days is used since t_d is larger than 1 for times greater than 33 days.

Chapter 6: Summary and Conclusions

The goal of this study was to better understand how oil recovery from naturally fractured oil-wet reservoirs depends on fracture spacing when surfactants are used to enhance imbibition into the matrix. A series of low IFT surfactant imbibition experiments were performed using cores with different dimensions to determine the effect of diameter and height on the oil recovery. The surfactant selection used in this study was the same approach that has been successfully used to identify the best surfactants for chemical flooding of non-fractured reservoirs. A dynamic imbibition cell was developed and used to measure the oil recovery, produced as emulsion, from carbonate cores. The emulsion was flushed out periodically to measure the oil recovery.

The scaling of gravity-dominated imbibition to core height and diameter (equivalent to vertical and horizontal fracture spacing) was studied. Most if not all previously published experiments were done using cores with a very small diameter of about 3.8 cm. The core diameters in this study varied from 3.8 to 20 cm. The oil recovery was lower for cores with a larger diameter and a larger height (vertical length). The oil recovery also decreased with higher IFT and lower surfactant concentration.

The experimental oil recovery data were compared with a new analytical imbibition model developed in Li et al. (2016) and Pope (2016) to test the model with respect to core dimensions and other parameters affecting the oil recovery. The new model took into account pressure gradients in both the horizontal and vertical directions. The model calculated oil recovery agreed remarkably well with the experimental data. Figure 5.7 shows the experimental oil recovery data plotted versus non-dimensional time, where non-dimensional time is defined based on the model as $t_d = \frac{2k_w k_{rw} \Delta\rho g H t}{\phi \mu_w (R^2 + MH^2)}$.

The experimental error based on the duplicate experiments is about 4% OOIP. The standard error of the difference between the experimental data and the model is 5.5% OOIP (Table 5.2). This agreement is excellent considering the variations in the experimental conditions: the diameter varied by a factor of 5, the height by a factor of 3, the permeability by a factor of 11, the microemulsion viscosity by a factor of 45, the porosity by a factor of 2, and the IFT by a factor of 100.

The microemulsion relative permeability used to fit the oil recovery data appear to be physically reasonable considering the low IFT condition. The model predicts a more complicated dependence on fracture spacing than predicted by previously published scaling groups. The predicted scaling also depends on the mobility ratio and time. The new model is limited to low IFT imbibition and has other significant limitations based on its idealizations. Nevertheless, the model is in good agreement with the experimental data over a wide range of conditions. The model provides a useful guide to a better understanding of how to scale up the process from the lab to the field.

Appendix A: Derivation of Imbibition Model

A.1 Derivation of Imbibition Model for a Cylindrical Core

Both Chen (2014) and Mirzaei et al. (2015) have derived analytical models of the low IFT imbibition process. The derivation of the new model (Li et al. 2016, Pope 2016) presented here builds on those previous attempts to understand the process in simple terms and account for the dominant driving forces under low IFT conditions. The following assumptions are made to derive the simplified model of surfactant imbibition into a cylindrical core:

1. Surfactant solution surrounds the core uniformly from the sides.
2. Uniform permeability, porosity, and initial oil saturation.
3. Low IFT (negligible capillary pressure) where there is surfactant present in the rock. Under these conditions, buoyancy is the driving force but a small pressure gradient exists in both the horizontal and vertical directions.
4. The volume of the produced oil is equal to the volume of surfactant solution imbibed (incompressible fluids and rock).
5. Surfactant solution invades horizontally from the sides and forms a microemulsion that displaces the oil vertically as depicted schematically in the diagram below.
6. Surfactant solution invades in proportion to the gravity head in the fracture forming a truncated cone until the surfactant reaches the center of the core. Mirzaei et al. (2015) show CT images of surfactant imbibition that suggest an invasion cone is a reasonable idealization.

7. k_{rw} and μ_w should be considered microemulsion properties since the surfactant mixes with the water and oil when it invades the rock from the fracture.
8. Uniform surfactant adsorption on the rock.
9. Neglect diffusion.

Consider a cylinder of radius R and height H as shown below:

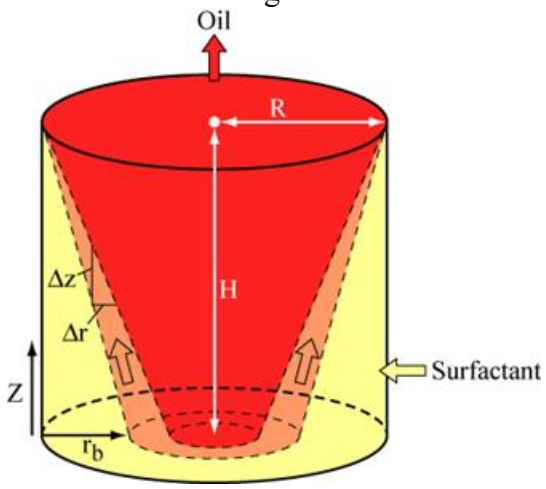


Figure A.1: Schematic of surfactant imbibition into a cylindrical core.

The surfactant solution invades from the sides of the core and mixes with the oil and brine to form a microemulsion. In general, the microemulsion will have a higher viscosity than the water, which causes a higher pressure gradient in the horizontal direction than would otherwise exist.

The approximate flow rate of the microemulsion in the triangular element shown above is given by:

$$q_w \cong 2\pi r \Delta z \frac{k_w}{\mu_w} \frac{\Delta P_w}{\Delta r}$$

The oil is displaced upward near the conical surface with an approximate flow rate given by:

$$q_o \cong 2\pi r \Delta r \frac{k_o}{\mu_o} \frac{\Delta P_o}{\Delta z}$$

Assume $q_w = q_o$ and solve for the ratio of pressure drops in the horizontal and vertical directions:

$$2\pi r \Delta z \frac{k_w}{\mu_w} \frac{\Delta P_w}{\Delta r} = 2\pi r \Delta r \frac{k_o}{\mu_o} \frac{\Delta P_o}{\Delta z}$$

$$\frac{\Delta P_w}{\Delta P_o} = \left(\frac{\Delta r}{\Delta z}\right)^2 \frac{k_o \mu_w}{k_w \mu_o}$$

The sum of the pressure drops is given by the buoyancy term:

$$\Delta P_w + \Delta P_o = g \Delta \rho H$$

The ratio of the pressure drops is roughly approximated as follows:

$$\frac{\Delta P_w}{\Delta P_o} = \left(\frac{R}{H}\right)^2 \frac{k_o \mu_w}{k_w \mu_o}$$

Using these two relationships, the horizontal flux at the base of the core when the surfactant has reached radius r_b is approximated as:

$$u_w = \frac{k_w (P_1 - P_2)}{\mu_w r_b} = \frac{\frac{k_w g \Delta \rho H}{r_b \mu_w}}{1 + \frac{k_w \mu_o}{k_o \mu_w}\left(\frac{H}{R}\right)^2} = \phi (1 - S_{orc} + D_s) \frac{dr_b}{dt}$$

Where D_s is the surfactant adsorption in units of surfactant volume per pore volume rock and S_{orc} is the average residual oil saturation to surfactant at low interfacial tension.

Separating variables and integrating assuming constant fluid properties:

$$r_b dr_b = \frac{\frac{k_w g \Delta \rho H}{\mu_w \phi (1 - S_{orc} + D_s)} dt}{\left[1 + \frac{k_w \mu_o}{k_o \mu_w}\left(\frac{H}{R}\right)^2\right]}$$

Divide r_b by the radius R of the core:

$$\frac{r_b}{R} = \sqrt{\frac{2k_w k_{rw} g \Delta\rho H t}{\mu_w \phi (1 - S_{orc} + D_s)(R^2 + MH^2)}}$$

Where the mobility ratio is defined as:

$$M = \frac{k_{rw}\mu_o}{k_{ro}\mu_w}$$

The oil recovery as a fraction of the initial oil in the core is given by:

$$\frac{\Delta V_o}{V_{oi}} = \left(\frac{r_b}{R} - \frac{1}{3}\left(\frac{r_b}{R}\right)^2\right)\left(1 - \frac{S_{or}}{S_{oi}}\right)$$

The model predicts the initial oil production is proportional to the square root of time due to the first term in the last equation. The scaling depends on both the geometry and the mobility ratio and changes with time.

A.2 Derivation of Imbibition Model for a Rectangular Block

The analogous derivation for a rectangular matrix block using the same assumptions as used for the cylindrical geometry proceeds in the same fashion.

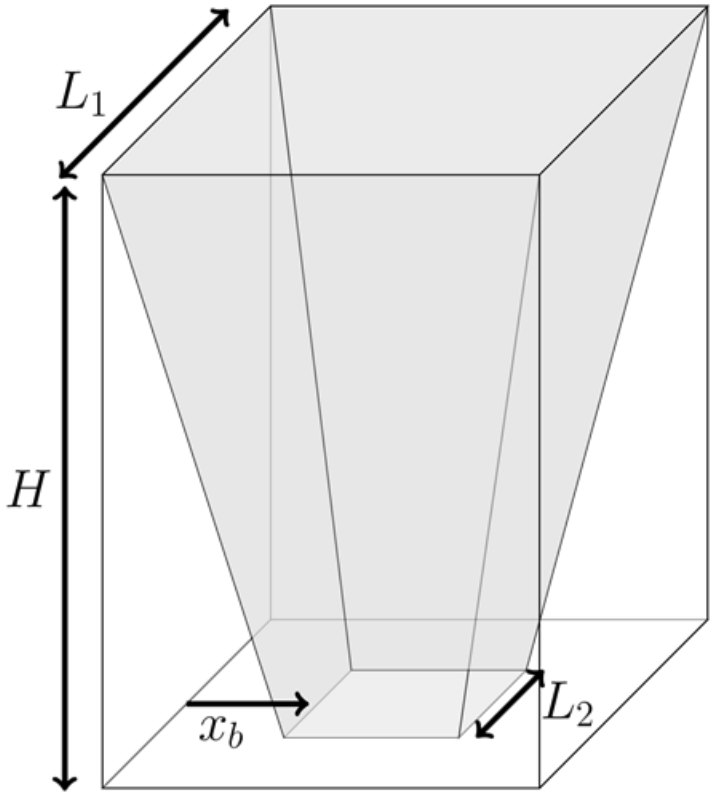


Figure A.2: Schematic of surfactant imbibition into a rectangular block.

The volume of a truncated pyramid is given by:

$$V_{TP} = (L_1^2 + L_1 L_2 + L_2^2)\frac{H}{3}$$

The total volume of the rectangular prism is given by:

$$V = L_1^2 H$$

The difference in volume is given by:

$$\Delta V = L_1^2 H - (L_1^2 + L_1 L_2 + L_2^2)\frac{H}{3}$$

Let

$$L_2 = L_1 - 2x_b$$

Where x_b is the surfactant invasion distance at the bottom of the rock:

$$\Delta V = L_1^2 H - \frac{H}{3}[L_1^2 + L_1(L_1 - 2x_b) + (L_1 - 2x_b)^2] = 2Hx_b L_1 - \frac{4Hx_b^2}{3}$$

$$\frac{\Delta V}{V} = \frac{2x_b}{L_1} - \frac{1}{3}\left(\frac{2x_b}{L_1}\right)^2 = \frac{x_b}{L/2} - \frac{1}{3}\left(\frac{x_b}{L/2}\right)^2$$

$$q_w = 4x\Delta z \frac{k_w}{\mu_w}\frac{\Delta P_w}{\Delta x}$$

$$q_o = 4x\Delta x \frac{k_o}{\mu_o}\frac{\Delta P_o}{\Delta z}$$

$$4x\Delta z \frac{k_w}{\mu_w}\frac{\Delta P_w}{\Delta x} = 4x\Delta x \frac{k_o}{\mu_o}\frac{\Delta P_o}{\Delta z}$$

Making the same assumptions as before:

$$\frac{\Delta P_w}{\Delta P_o} = \left(\frac{\Delta x}{\Delta z}\right)^2 \frac{k_o \mu_w}{k_w \mu_o} = \frac{k_o \mu_w}{k_w \mu_o}\left(\frac{L/2}{H}\right)^2$$

$$u_w = \frac{k_w(P_1 - P_2)}{\mu_w x_b} = \frac{k_w g \Delta\rho H}{\mu_w x_b}\frac{1}{\frac{k_w \mu_o}{k_o \mu_w}\left(\frac{H}{L/2}\right)^2 + 1} = \phi(1 - S_{or} + D_s)\frac{dx_b}{dt}$$

$$x_b^2 = \frac{\frac{2k_w g \Delta\rho H}{\mu_w x_b \phi(1 - S_{orc} + D_s)}}{1 + \frac{k_w \mu_o}{k_o \mu_w}\left(\frac{H}{L/2}\right)^2}$$

$$\frac{x_b}{L/2} = \sqrt{\frac{2k_w k_{rw} g \Delta\rho H t}{\mu_w \phi(1 - S_{orc} + D_s)\left[\left(\frac{L}{2}\right)^2 + MH^2\right]}}$$

The oil recovery as a fraction of the initial oil is given by:

$$\frac{\Delta V_o}{V_{oi}} = \left[\frac{x_b}{L/2} - \frac{1}{3}\left(\frac{x_b}{L/2}\right)^2\right]\left(1 - \frac{S_{or}}{S_{oi}}\right)$$

This is equivalent to the cylindrical case.

Nomenclature

D_s	Surfactant adsorption in pore volumes
g	Gravitational acceleration constant
H	Height of cylindrical core or rectangular matrix block
k_w	Brine permeability at 100% brine saturation
k_{ro}	Oil relative permeability
k_{rw}	Microemulsion relative permeability
L_1	Length of side of rectangular block
L_2	Horizontal length of inverted truncated pyramid used in model
L_c	Scaling length
L_x	Fracture spacing in horizontal x-direction
L_y	Fracture spacing in horizontal y-direction
M	Mobility ratio
P_o	Pressure in oil phase
P_w	Pressure in water phase
q_o	Volumetric flow rate of oil phase
q_w	Volumetric flow rate of water phase
r	Radius of invasion
r_b	Radius of invasion at the bottom of the core
R	Radius of cylindrical core
S_{oi}	Initial oil saturation
S_{or}	Residual oil saturation
S_{orc}	Residual oil saturation after chemical flood
t	Time

t_d	Non-dimensional time
u_w	Darcy velocity of water phase
ΔV_o	Volume of oil produced
V_{oi}	Volume of initial oil in place
x	Horizontal distance of surfactant invasion
x_b	Horizontal distance of surfactant invasion at the base of the core

Greek Symbols

μ_o	Oil viscosity
μ_w	Water or microemulsion viscosity
ρ_o	Oil density
ρ_w	Water or microemulsion density
ϕ	Porosity

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